Supporting Information for

Solvent-Controlled, Chemodivergent Oxidative Anionic Fries Rearrangement of *O*-Aryl Carbamates Under Aerobic Conditions

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Experimental details

SAFETY NOTE: Organolithiums were handled under an inert atmosphere (Schlenk techniques) until the point at which they were mixed with a solution of the substrate in 2-MeTHF, under an air atmosphere and with vigorous magnetic stirring, whereupon they react quickly. No particular problems were experienced during the addition. Organolithiums, however, are notoriously prone to ignition in air, and caution should be exercised in adopting the recommended procedure, especially on a larger scale.

Materials and methods. Unless specified, all reagents were used as received without further purifications. Anhydrous tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MeTHF), cyclopentyl methyl ether (CPME) and 4-methyltetrahydropyran (4-MeTHP), 1,2-dimethoxyethane (DME) and methyl *t*-butyl ether (MTBE) were distilled under nitrogen over Na/benzophenone ketyl prior to use. Reactions were monitored by GC-MS analysis or by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminium plates (60 Merck F254) with UV light (254 nm) as visualizing agent. Chromatographic separations were carried out under pressure on silica gel (40-63 μm, 230-400 mesh) using flash-column techniques. The following solutions of organolithium reagents were furnished by Merck-Aldrich with the following concentration: *n*-BuLi 2.5 M in hexanes, *s*-BuLi 1.4 M in cyclohexane, *t*-BuLi 1.6 M in pentane. The exact concentration of the organolithium solutions was determined by titration with diphenylacetic acid in anhydrous THF prior to use.[1] Anhydrous 2,2,6,6-tetramethylpiperidine (TMP) and *N*,*N*-diisopropylamine (DA) were dried over CaH_2, distilled under reduced pressure (60 mmHg) prior to use, and stored under inert atmosphere. Full characterisation data, including copies of ^{1}H and ^{13}C NMR spectra of new compounds, have been reported.

Preparation of 1 M lithium tetramethylpiperidide (LiTMP) solution in 2-MeTHF. In a Schlenk flask under a positive nitrogen pressure, *n*-BuLi (2.5 M in hexanes, 4.0 mmol, 1.0 eq.) was added to a precooled (0 °C) stirred solution of 2,2,6,6-tetramethylpiperidine (TMP) (4.4 mmol, 1.1 eq., 0.75 mL) in 2-MeTHF (1.65 mL). The mixture was stirred at 0 °C for 10 min to yield a clear yellow solution of LiTMP that was used without further purification.

Preparation of 1 M lithium diisopropylamide (LDA) solution in 2-MeTHF. In a Schlenk flask under a positive nitrogen pressure, *n*-BuLi (2.5 M in hexanes, 4.0 mmol, 1.0 eq.) was added to a precooled (0 °C) stirred solution of diisopropylamine (4.4 mmol, 1.1 eq., 1 M in dry 2-MeTHF). The mixture was stirred at 0 °C for 10 min to yield a clear solution of LDA that was used without further purifications.

Instrumentation. ^{1}H NMR (600 MHz), $^{13}C\{^{1}H\}$ (150 MHz), ^{19}F (564 MHz) NMR spectra were recorded on a Jeol ECZR600 or on a Bruker AVANCE 400 spectrometer (^{1}H NMR 400 MHz, $^{13}C\{^{1}H\}$ 100 MHz) at room temperature using residual solvent peak as an internal reference. ^{2}H NMR (92.07 MHz) spectra were obtained in CH_2Cl_2 using residual CD_2Cl_2 as an internal standard. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) in Hertz (Hz). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), non (nonuplet), m (multiplet), br (broad).

Low-resolution MS spectra were recorded at an ionizing voltage of 70 eV on a HP 5989B mass selective detector connected to an HP 5890 GC with a methyl silicone capillary column (EI). The MS flow- injection analyses were run on a high resolving power hybrid mass spectrometer (HRMS) Orbitrap Fusion (Thermo Scientific, Rodano, Italy), equipped with an ESI ion source. The samples were analyzed in acetonitrile solution using a syringe pump at a flow rate of 5 μL/min. The tuning parameters adopted for the ESI source were: source voltage 4.0 kV. The heated capillary temperature was maintained at 275 °C. The mass accuracy of the recorded ions (vs. the calculated ones) was ± 2.5 mmu (milli-mass units). Analyses were run using both full MS (150-2000 *m/z* range) and MS/MS acquisition, at 500000 resolutions (200 *m/z*).

n-Heptane was used as the internal standard (ISTD) for quantitative ^{1}H NMR analysis of the crude reaction mixtures. The amount of product was determined by applying the following equation:

$$Equation\ (1): \qquad yield\ (\%) = \frac{x\ (product) \cdot n\ (ISTD)}{n(starting\ material)} \cdot f \cdot 100$$

where:

x is the value of integral/number of protons;

n is the amount of the starting material and of internal standard (ISTD) in mmol;

f the diluting factor used for the preparation of the sample.

Synthesis and analysis of *O*-aryl carbamates **1a-1ad**

General procedure A. To a stirred solution of the appropriate phenol (1.0 eq.) in anhydrous pyridine (1 M) under positive nitrogen pressure, the corresponding carbamoyl chloride (1.0 eq.) was added. The resulting reaction mixture was heated to reflux and stirred overnight. The mixture was allowed to cool to room temperature and then Et_2O and 1 M HCl were added. After extraction with Et_2O, the organic layer was washed with aqueous 2 M HCl (3 x 20 mL) and aqueous 1 M NaOH (2 x 20 mL), dried over Na_2SO_4 and concentrated under vacuum. When necessary, the resulting crude material was purified by flash column chromatography on silica gel.

General procedure B.[2] To a stirred solution of *N,N'*-carbonyldiimidazole (CDI) (1.1 eq.) in THF (0.5 M) or CH_2Cl_2 (1 M) was added the selected amine (1.0 eq.). The resulting mixture was heated to reflux and stirred overnight. After completion, as monitored by TLC analysis, the mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting crude material was dissolved in CH_2Cl_2 (25 mL) and washed with water (3 x 25 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the corresponding carbamoylimidazole, which was used in the following step without any further purification. To a stirred solution of carbamoylimidazole (1.0 eq.) in acetonitrile (0.5 M), iodomethane (4.0 eq.) was added. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to yield the corresponding carbamoylimidazolium salt, which was used in the following step without any further purification. To a stirred solution of the crude carbamoylimidazolium salt (1.0 eq.) in acetonitrile (0.2 M), *ortho*-cresol (1.0 eq.) and triethylamine (1.0 eq.) were added. The reaction mixture was heated to reflux and stirred overnight. After allowing to cool to room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 (20 mL). The organic layers were washed with aqueous 0.1 M HCl (3 x 25 mL), brine (3 x 25 mL) and aqueous 0.1 M NaOH (3 x 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the corresponding carbamate. When necessary, the resulting crude material was purified by flash column chromatography on silica gel.

General procedure C.[3] To a stirred solution of the selected amine (1.0 eq.) and triethylamine (1.2 eq.) in benzene at 0 °C, triphosgene (0.34 eq.) was slowly added. The reaction mixture was stirred overnight at room temperature and then quenched with aqueous 1 M HCl. The mixture was extracted with CH_2Cl_2 (3 x 20 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give the corresponding carbamoyl chloride, which was used without any further purification. To a stirred solution of the carbamoyl chloride (1 eq.) in anhydrous pyridine (0.5 M), *ortho*-cresol (1 eq.) was added. The reaction mixture was refluxed overnight and then quenched with aqueous 2 M HCl. The mixture was extracted with Et_2O (3 x 20 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel gave the corresponding carbamate. When necessary, the resulting crude material was purified by flash column chromatography on silica gel.

General procedure D.[4] To a stirred solution of the appropriate *N,N*-diisopropylcarbamate (1.0 eq.) in anhydrous THF (0.2 M) under nitrogen at –78 °C, *t*-BuLi (1.6 M in pentane, 2.0 eq.) was added dropwise. After stirring 1 h at -78 °C, the selected electrophile (2.5 eq.) was added, and the reaction was allowed to warm to room temperature overnight. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc (3 x 10 mL) and the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The resulting crude material was purified by flash column chromatography.

2,4-Dimethylphenyl-*N,N*-diisopropylcarbamate (1a): General procedure **A** starting from 2,4-dimethylphenol (1.0 eq., 10.0 mmol, 1.20 mL) and *N,N*-diisopropylcarbamoyl chloride (1.0 eq., 10.0 mmol, 1.64 g) gave **1a** as a colourless semisolid (1.87 g. 75%), which was used without any further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 2.2 Hz, 1H), 6.97 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 4.08 (br s, 1H) superimposed to 4.00 (br s, 1H), 2.29 (s, 3H), 2.17 (s, 3H), 1.35 (br s, 6H) superimposed to 1.28 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.9, 147.9, 134.9, 131.7, 130.3, 127.4, 122.1, 46.9, 46.2, 21.7, 20.9, 20.7, 16.5. EI-MS *m/z* (%): 249 (M^+, 5), 128 (73), 122 (74), 107 (23), 86 (100), 43 (48). All analytical data were in good accordance with those reported in the literature.[4]

2-Methyl-*N,N*-diisopropylcarbamate (1b): General procedure **A** starting from *ortho*-cresol (1.0 eq., 10.0 mmol, 1.0 mL) and *N,N*-diisopropylcarbamoyl chloride (1.0 eq., 10.0 mmol, 1.64 g) gave **1b** as a colourless semisolid (1.42 g, 60 %), which was used without any further purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.4 Hz, 1H), 7.18 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 7.04 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.08 (br s, 1H) superimposed to 4.03 (br s, 1H), 2.22 (s, 3H), 1.36 (br s, 6H) superimposed to 1.30 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.7, 150.1, 131.1, 130.8, 126.9, 125.4, 122.4, 46.9, 46.3, 21.7, 20.6, 16.6. All analytical data were in good accordance with those reported in the literature.[4]

4-Chloro-2-methylphenyl-*N,N*-diisopropylcarbamate (1c): General procedure **D** starting from 4-chlorophenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 3.92 mmol, 1.0 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 7.84 mmol, 4.90 mL) and iodomethane (2.5 eq., 9.80 mmol, 0.61 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1c** as a yellow liquid (0.52 g, 49%, R_f = 0.35 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 2.6 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.04 (br s, 2H), 2.19 (s, 3H), 1.34 (br s, 6H) superimposed to 1.29 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, CDCl3) δ 153.3, 148.7, 132.7, 130.8, 130.4, 126.8, 123.7, 47.0, 46.4, 21.7, 20.6, 16.6. EI-MS *m/z* (%): 269 (M^+, 1), 142 (46), 128 (84), 107 (19), 86 (100), 43 (48). All analytical data were in good accordance with those reported in the literature.[4]

2-Methyl-4-iodophenyl-*N,N*-diisopropylcarbamate (1d): General procedure **A** starting from 2-methyl-4-iodophenol (1.0 eq., 10.0 mmol, 2.34 g) and *N,N*-diisopropylcarbamoyl chloride (1.0 eq., 10.0 mmol, 1.64 g); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1d** as a colourless solid (2.6 g, 72%, R_f = 0.25 petroleum ether/Et_2O 9/1 v/v), mp. 57.1-59.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H), 7.48 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.03 (s, 2H), 2.17 (s, 3H), 1.33 (br s, 6H) superimposed to 1.29 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.1, 150.1, 139.8, 135.9,

133.5, 124.5, 89.4, 47.0, 46.4, 21.7, 20.6, 16.3. HRMS (ESI): *m/z* calcd for $C_{14}H_{20}INO_2 + H^+$: 362.0612 [M+H$^+$]; found 362.0623.

2-Methyl-4-(trifluoromethyl)phenyl-*N,N*-diisopropylcarbamate (1e): General procedure **D** starting from 4-(trifluoromethyl)phenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 3.46 mmol, 1.0 g). *t*-BuLi (1.6 M in pentane, 2.0 eq., 4.33 mL) and iodomethane (2.5 eq., 8.65 mmol, 0.55 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1e** as a colourless liquid (0.90 g, 86%, R_f = 0.50 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.1 Hz, 1H), 7.45 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 4.05 (sept, *J* = 6.2 Hz, 2H), 2.27 (s, 3H), 1.36 (br d, *J* = 6.9 Hz, 6H) superimposed to 1.31 (br d, *J* = 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) δ 152.9, 152.7, 131.7, 128.2 (q, *J* = 3.6 Hz, 1C), 127.6 (q, *J* = 32.2 Hz, 1C), 124.2 (q, *J* = 272.0 Hz, 1C), 124.1 (q, *J* = 4.3 Hz, 1C), 122.9, 47.1, 46.6, 21.7, 20.6, 16.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.01 (s, 3F). EI-MS *m/z* (%): 303 (M$^+$, 1), 176 (44), 128 (85), 86 (100), 43 (55). All analytical data were in good accordance with those reported in the literature.[4]

2-Methyl-4-methoxyphenyl-*N,N*-diisopropylcarbamate (1f): General procedure **D** starting from 4-methoxyphenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 3.98 mmol, 1.0 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 7.96 mmol, 4.98 mL) and iodomethane (2.5 eq., 9.95 mmol, 0.62 mL) gave **1f** as a yellow liquid (0.89 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.7 Hz, 1H), 6.74 (d, *J* = 3.0 Hz, 1H), 6.71 (dd, *J* = 8.7, 3.1 Hz, 1H), 4.06 (br s, 2H), 3.77 (s, 3H), 2.18 (s, 3H), 1.34 (br s, 6H) superimposed to 1.29 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 156.7, 153.9, 143.6, 131.6, 122.8, 116.1, 111.7, 55.5, 46.7, 46.0, 21.5, 20.5, 16.7. EI-MS *m/z* (%): 265 (M$^+$, 9), 138 (70), 128 (59), 123 (32), 86 (100), 43 (55). All analytical data were in good accordance with those reported in the literature.[5]

2-Methyl-6-methoxyphenyl-*N,N*-diisopropylcarbamate (1g): General procedure **A** starting from 2-methoxy-6-methylphenol (1.0 eq., 5.0 mmol, 0.69 g) and *N,N*-diisopropylcarbamoyl chloride (1.0 eq., 5.0 mmol, 0.82 g) gave **1g** as a colorless solid (1.84 g, 69%), mp. 50.5-54.5 °C, without any purification. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.9 Hz, 1H), 6.81-6.77 (m, 2H), 4.15 (br s, 1H) superimposed to 3.95 (br s, 1H), 3.79 (s, 3H), 2.21 (s, 3H), 1.37 (br s, 6H) superimposed to 1.28 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.6, 152.1, 139.4, 132.3, 125.4, 122.6, 110.0, 56.1, 47.0, 46.1, 21.7, 20.7, 16.3. All analytical data were in good accordance with those reported in the literature.[4]

2-Methyl-4-(methylthio)phenyl-*N,N*-diisopropylcarbamate (1h): General procedure **D** starting from 4-(methylthio)phenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 3.75 mmol, 1.0 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 7.50 mmol, 4.69 mL) and iodomethane (2.5 eq., 9.38 mmol, 0.58 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1h** as a yellow liquid (0.90 g, 86%, R_f = 0.38 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 2.1 Hz, 1H), 7.10 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.04 (br s, 2H), 2.45 (s, 3H), 2.19 (s, 3H), 1.34 (br s, 6H) superimposed to 1.29 (br s, 6H). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.6, 148.1, 134.6, 131.4, 130.2, 126.0, 122.9, 47.0,

46.3, 21.7, 20.6, 17.0, 16.6. EI-MS *m/z* (%): 281 (M^+, 23), 154 (81), 139 (28), 128 (79), 86 (100), 43 (49). All analytical data were in good accordance with those reported in the literature.[4]

4-Methylbenzo[d][1,3]dioxol-5-yl-*N,N*-diisopropylcarbamate (1i): General procedure **D** starting from benzo[d][1,3]dioxol-5-yl-*N,N*-diisopropylcarbamate[6] (1.0 eq., 1.90 mmol, 0.50 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 3.80 mmol, 2.38 mL) and iodomethane (2.5 eq., 4.75 mmol, 0.30 mL); purification by flash chromatography on silica gel (petroleum ether/Et_2O 85/15 v/v) gave **1i** as a white solid (0.43 g, 81%, R_f = 0.23 petroleum ether/Et_2O 85/15 v/v), mp. 105.4-107.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.51 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 2H), 4.06 (br s, 1H) superimposed to 4.0 (br s, 1H), 2.07 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 6H) superimposed to 1.28 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.8, 146.5, 144.8, 144.2, 114.4, 113.8, 105.2, 101.3, 46.8, 46.1, 21.5, 20.5, 9.5. HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NO_4$ + Na^+: 302.1363 [M+Na^+]; found 302.1360.

3-Methyl-[1,1'-biphenyl]-4-yl-*N,N*-diisopropylcarbamate (1j): General procedure **D** starting from [1,1'-biphenyl]-4-yl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 3.37 mmol, 1.0 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 6.74 mmol, 4.21 mL) and iodomethane (2.5 eq., 8.43 mmol, 0.52 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1j** as a white solid (0.87 g, 83%, R_f = 0.25 petroleum ether/Et_2O 9/1 v/v), mp. 84.0-85.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.45-7.39 (m, 4H), 7.35-7.31 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 4.08 (br s, 2H), 2.29 (s, 3H), 1.38 (br s, 6H) superimposed to 1.32 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, CDCl3) δ 153.7, 149.6, 141.0, 138.6, 131.0, 130.0, 128.8, 127.3, 127.2, 125.7, 122.7, 47.0, 46.4, 21.7, 20.7, 16.8. EI-MS *m/z* (%): 311 (M^+, 10), 184 (85), 128 (95), 86 (100), 43 (42). All analytical data were in good accordance with those reported in the literature.[4]

2-Methylnaphtalen-1-yl-*N,N*-diisopropylcarbamate (1k): General procedure **D** starting from naphtalen-1-yl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 3.69 mmol, 1.0 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 7.38 mmol, 4.61 mL) and iodomethane (2.5 eq., 9.23 mmol, 0.57 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 98/2 v/v) gave **1k** as a yellow solid (0.75 g, 71%, R_f = 0.18, petroleum ether/Et_2O 98/2 v/v), mp. 97.4-100.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.48 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 4.19-4.16 (m, 2H), 2.37 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.3, 144.8, 133.2, 128.8, 128.1, 127.8, 126.9, 126.3, 125.2, 125.1, 121.1, 47.0, 46.2, 21.8, 20.6, 16.6. HRMS (ESI): *m/z* calcd for $C_{18}H_{23}NO_2$ + H^+: 286.1802 [M+H^+]; found 286.1811.

2-Methyl-4-(phenylselanyl)phenyl-*N,N*-diisopropylcarbamate (1l): General procedure **D** starting from 4-(phenylselanyl)phenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 0.60 mmol, 0.21 g), *t*-BuLi (1.6 M in pentane, 2.0 eq., 1.20 mmol, 0.75 mL) and iodomethane (2.5 eq., 1.50 mmol, 0.10 mL); purification by flash chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1l** as a colourless oil (0.19 g, 79%, R_f = 0.38 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.40-7.38 (m, 1H), 7.35-7.31 (m, 1H), 7.26-7.21 (m, 3H), 6.97 (d, *J* = 8.2 Hz, 1H), 4.04 (br s, 2H), 2.18 (s, 3H), 1.34 (br s, 6H) superimposed to 1.29 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.2, 149.8, 140.1, 136.5, 132.5, 132.0, 132.0, 129.2,

126.9, 126.2, 123.3, 46.8, 46.3, 21.5, 20.5, 16.4. HRMS (ESI): *m/z* calcd for $C_{20}H_{25}NO_2Se + H^+$: 392.1223 [M+H$^+$]; found 392.1229.

2-Methyl-4-styrylphenyl-*N,N*-diisopropylcarbamate (1m): to a degassed solution of 2-methyl-4-iodophenyl-*N,N*-diisopropylcarbamate **1d** (1.0 eq., 2.0 mmol, 0.72 g) in anhydrous DMF (10 mL, 0.2 M), tetrabutylammonium bromide (TBAB) (0.4 eq., 0.80 mmol, 0.26 g), *n*-Bu_3N (2.0 eq., 4.0 mmol, 0.95 mL), $Pd(OAc)_2$ (0.10 eq., 0.20 mmol, 0.045 g), tri-*o*-tolyl phosphine (0.2 eq., 0.40 mmol, 0.12 g) and styrene (2.0 eq., 4.0 mmol, 0.42 g) were sequentially added. The reaction mixture was stirred overnight at 100 °C. After completion (16 h), the reaction mixture was cooled to room temperature, washed with saturated aqueous NH_4Cl and filtered on a celite pad. Water was added and the reaction mixture was extracted with EtOAc (3 x 10 mL), dried over Na_2SO_4 and concentrated under vacuum. The resulting crude material was purified by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) to give **1m** as a white solid (0.46 g, 68%, R_f = 0.30 petroleum ether/Et_2O 9/1 v/v), mp. 103.6-106.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.39-7.32 (m, 4H), 7.26-7.22 (m, 1H), 7.07 (d, *J* = 16.3 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H) superimposed to 7.02 (d, *J* = 16.3 Hz, 1H), 4.08 (br s, 1H) superimposed to 4.03 (br s, 1H), 2.25 (s, 3H), 1.37 (br s, 6H) superimposed to 1.30 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.4, 149.5, 137.4, 134.5, 130.8, 129.0, 128.6, 128.1, 127.4, 126.4, 124.9, 122.5, 46.8, 46.2, 21.5, 20.7, 20.5, 16.6, 14.0. EI-MS *m/z* (%): 337 (M$^+$, 12), 210 (38), 128 (70), 86 (100). HRMS (ESI): *m/z* calcd for $C_{22}H_{27}NO_2 + H^+$: 338.2115 [M+H$^+$]; found 338.2122.

2-Methyl-4-(phenylethynyl)phenyl-*N,N*-diisopropylcarbamate (1n): to a degassed solution of 2-methyl-4-iodophenyl-*N,N*-diisopropylcarbamate **1d** (1.0 eq., 2.0 mmol, 0.72 g) in anhydrous THF (10 mL, 0.2 M), anhydrous triethylamine (1.3 eq., 2.6 mmol, 0.36 mL), $PdCl_2(PPh_3)_2$ (0.025 eq., 0.05 mmol, 35 mg), CuI (0.06 eq., 0.12 mmol, 23 mg) and phenylacetylene (1.3 eq., 2.6 mmol, 0.29 mL), were sequentially added. The reaction mixture was stirred at room temperature overnight. After completion, saturated aqueous NH_4Cl was added and the reaction mixture was extracted with EtOAc (3 x 10 mL), dried over Na_2SO_4 and concentrated under vacuum. The resulting crude material was purified by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) to give **1n** as a yellow solid (0.65 g, 97% R_f = 0.18, petroleum ether/Et_2O 9/1 v/v), mp. 114.2-115.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.40-7.42 (m, 1H), 7.38-7.30 (m, 4H), 7.04 (d, *J* = 8.3 Hz, 1H), 4.06 (br s, 2H), 2.22 (s, 3H), 1.35 (br s, 6H) superimposed to 1.31 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.1, 150.0, 134.2, 131.5, 130.7, 130.1, 128.3, 128.1, 123.4, 122.4, 120.1, 89.1, 88.7, 46.8, 46.2, 21.5, 20.5, 16.3. EI-MS *m/z* (%): 335 (M$^+$, 8), 208 (57), 128 (80), 86 (100). HRMS (ESI): *m/z* calcd for $C_{22}H_{25}NO_2 + H^+$: 336.1958 [M+H$^+$]; found 336.1965.

4-(Methoxymethoxy)-2-methylphenyl-*N,N*-diisopropylcarbamate (1o): General procedure **D** starting from 4-(methoxymethoxy)phenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 0.80 mmol, 0.23 g),), *t*-BuLi (1.6 M in pentane, 2.0 eq., 1.60 mmol, 1.0 mL) and iodomethane (2.5 eq., 2.0 mmol, 0.12 mL); purification by flash chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1o** as a colourless liquid (0.20 g, 83%, R_f = 0.33 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.7 Hz, 1H), 6.89 (d, *J* = 2.8 Hz, 1H), 6.85 (dd, *J* = 8.7, 3.0 Hz, 1H), 5.13 (s, 2H), 4.06 (br s, 1H) superimposed to 4.01 (br s, 1H), 3.46 (s, 3H), 2.18 (s, 3H), 1.34 (br s, 6H) superimposed to 1.28 (br s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 154.6,

153.9, 144.7, 131.9, 123.1, 118.7, 114.5, 94.9, 56.0, 46.9, 46.2, 21.7, 20.7, 16.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_4 + H^+$: 296.1856 [M+H$^+$]; found 296.1861.

2-Methyl-6-(trimethylsilyl)phenyl-*N,N*-diisopropylcarbamate (1p): General procedure **D** starting from 2-(trimethylsilyl)phenyl-*N,N*-diisopropylcarbamate[4] (1.0 eq., 1.06 mmol, 0.32 g),), *t*-BuLi (1.6 M in pentane, 2.0 eq., 2.12 mmol, 1.33 mL) and iodomethane (2.5 eq., 2.65 mmol, 0.16 mL); purification by flash chromatography on silica gel (petroleum ether/Et_2O 95/5 v/v) gave **1p** as a white solid (0.20 g, 60%, R_f = 0.31 petroleum ether/Et_2O 95/5 v/v), mp. 82.0-84.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (ddd, *J* = 7.3, 1.8, 0.7 Hz, 1H), 7.21 (ddt, *J* = 7.4, 1.7, 0.8 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.57 (sept, *J* = 6.8 Hz, 1H), 3.58 (sept, *J* = 6.8 Hz, 1H), 2.15 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.36 (d, *J* = 6.5 Hz, 3H), 1.29 (d, *J* = 6.1 Hz, 6H), 0.27 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 154.9, 152.0, 132.7, 132.5, 132.3, 130.6, 125.3, 47.8, 45.5, 21.3, 20.9, 20.8, 20.5, 16.7, -0.56. HRMS (ESI): *m/z* calcd for $C_{17}H_{29}NO_2Si + H^+$: 308.2040 [M+H$^+$]; found 308.2050.

4-Allyl-2-methoxy-6-methylphenyl-*N,N*-diisopropylcarbamate (1q): General procedure **A** starting from 4-allyl-2-methoxy-6-methylphenol[7] (1.0 eq., 3.0 mmol, 0.50 g) and *N,N*-diisopropylcarbamoyl chloride (1.0 eq., 3.0 mmol, 0.49 g); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 8/2 v/v) gave **1q** as a white solid (0.55 g, 60%, R_f = 0.25 petroleum ether/Et_2O 8/2 v/v), mp. 64.3-65.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.63-6.61 (m, 1H), 6.60-6.59 (m, 1H), 5.95 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.09 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.05 (dq, *J* = 10.0, 1.7 Hz, 1H), 4.15 (br s, 1H), 3.94 (br s, 1H), 3.78 (s, 3H), 3.32 (dt, *J* = 6.7, 1.5, 2H), 2.18 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 6H) superimposed to 1.27 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.6, 151.8, 137.7, 137.6, 137.3, 131.9, 122.6, 115.8, 110.4, 56.1, 47.0, 46.1, 40.3, 21.7, 20.7, 16.3. HRMS (ESI): *m/z* calcd for $C_{18}H_{27}NO_3 + H^+$: 306.2064 [M+H$^+$]; found 306.2070.

2-Methylbenzyl-*N,N*-diisopropylcarbamate (1r): General procedure **A** starting from *o*-tolylmethanol (1.0 eq., 5.0 mmol, 0.61 g) and *N,N*-diisopropylcarbamoyl chloride (1.0 eq., 5.0 mmol, 0.82 g); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 95/5 v/v) gave **1r** as a colourless oil (0.95 g, 77%, R_f = 0.40 petroleum ether/Et_2O 95/5 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.25-7.17 (m, 3H), 5.14 (s, 2H), 4.14-3.68 (m, 2H), 2.36 (s, 3H), 1.26-1.15 (m, 12H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.6, 136.8, 135.2, 130.3, 129.0, 128.2, 126.0, 65.0, 46.3, 20.8, 19.1. HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_2 + H^+$: 250.1802 [M+H$^+$]; found 250.1802.

2-Methylphenyl-*N,N*-diethylcarbamate (1s): General procedure **A** starting from *ortho*-cresol (1.0 eq., 3.0 mmol, 0.31 mL) and *N,N*-diethylcarbamoyl chloride (1.0 eq., 3.0 mmol, 0.38 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1s** as a colourless oil (0.28 g, 45%, R_f = 0.27 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.15 (m, 2H), 7.13-7.04 (m, 2H), 3.47 (q, *J* = 7.2 Hz, 2H) superimposed to 3.40 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H) superimposed to 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.1, 150.2, 131.1, 130.6, 126.89 125.5, 122.3, 42.4, 42.0, 16.4, 14.4, 13.6. HRMS (ESI): *m/z* calcd for $C_{12}H_{17}NO_2 + H^+$: 208.1332 [M+H$^+$]; found 208.1338. All analytical data were in good accordance with those reported in the literature.[8]

2-Methyl-*N*,*N*-dipropylcarbamate (1t): According to general procedure **B** in THF starting from dipropylamine (1.0 eq, 5.0 mmol, 0.68 mL), CDI (1.1 eq., 5.5 mmol, 0.89 g), iodomethane (4.0 eq., 18.4 mmol, 1.1 mL) in MeCN, *ortho*-cresol (1.0 eq., 4.8 mmol, 0.50 mL) and triethylamine (1.0 eq, 4.8 mmol, 0.70 mL) in MeCN; purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1t** as a yellow oil (0.88 g, 75%, R_f = 0.30 petroleum ether/Et_2O 9/1 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.25-7.14 (m, 2H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.38 (t, *J* = 7.5 Hz, 2H) superimposed to 3.31 (t, *J* = 7.3 Hz, 2H), 2.23 (s, 3H), 1.72 (sext, *J* = 7.4 Hz, 2H) superimposed to 1.65 (sext, *J* = 7.6 Hz, 2H), 0.96 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 154.6, 150.2, 131.0, 130.5, 126.8, 125.4, 122.3, 49.5, 49.3, 22.1, 21.3, 16.4, 11.4, 11.3. HRMS (ESI): *m/z* calcd for $C_{14}H_{21}NO_2 + H^+$: 236.1645 [M+H^+]; found 236.1649.

2-Methylphenyl-*N*,*N*-dibutylcarbamate (1u): According to general procedure **B** in THF starting from dibutylamine (1.0 eq., 6.0 mmol, 1.0 mL), using CDI (1.1 eq., 6.6 mmol, 1.07 g), iodomethane (4.0 eq., 21.5 mmol, 1.34 mL), *ortho*-cresol (1.0 eq., 5.34 mmol, 0.55 mL) and triethylamine (1.0 eq., 5.34 mmol, 0.74 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 95/5 v/v) gave **1u** as a colourless oil (0.96 g, 61%, R_f = 0.18 petroleum ether/Et_2O 95/5 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.22-7.16 (m, 2H), 7.09 (td, *J* = 7.4, 1.3 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.39 (t, *J* = 7.6 Hz, 2H), 3.32 (t, *J* = 7.5 Hz, 2H), 2.21 (s, 3H), 1.66 (quint, *J* = 7.9 Hz, 2H), 1.60 (quint, *J* = 7.6 Hz, 2H), 1.36 (m, 4H), 0.96 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 154.5, 150.2, 131.1, 130.6, 126.9, 125.4, 122.3, 47.6, 47.4, 31.1, 30.3, 20.2, 20.2, 16.5, 14.0, 14.0. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_2 + H^+$: 264.1958 [M+H^+]; found 264.1963.

2-Methylphenyl-*N*,*N*-diisobutylcarbamate (1v): According to general procedure **B** in THF starting from diisobutylamine (1.0 eq., 6.0 mmol, 1.1 mL), using CDI (1.1 eq., 6.6 mmol, 1.07 g), iodomethane (4.0 eq., 17.7 mmol, 1.1 mL), *ortho*-cresol (1.0 eq., 4.28 mmol, 0.44 mL) and triethylamine (1.0 eq., 4.28 mmol, 0.59 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 95/5 v/v) gave **1v** as a colourless oil (0.81 g, 52%, R_f = 0.18 petroleum ether/Et_2O 95/5 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.22-7.16 (m, 2H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 7.02 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.26 (d, *J* = 7.6 Hz, 2H), 3.18 (d, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 2.08 (m, 2H), 0.98 (d, *J* = 6.7 Hz, 6H), 0.93 (d, *J* = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 155.1, 150.3, 131.1, 130.6, 126.9, 125.5, 122.3, 55.3, 55.2, 27.7, 27.0, 20.3, 20.2, 16.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_2 + H^+$: 264.1958 [M+H^+]; found 264.1963.

2-Methylphenyl-*N*-cyclohexyl-*N*'-ethylcarbamate (1w): According to general procedure **B** in THF starting from *N*-ethylcyclohexylamine (1.0 eq., 6.0 mmol, 0.9 mL), using CDI (1.1 eq., 6.6 mmol, 1.07 g), iodomethane (4.0 eq., 20.7 mmol, 1.29 mL), *ortho*-cresol (1.0 eq., 4.96 mmol, 0.51 mL) and triethylamine (1.0 eq., 4.96 mmol, 0.69 mL); purification by flash column chromatography on silica gel (petroleum ether/Acetone 85/15 v/v) gave **1w** as a yellow oil (0.95 g, 61%, R_f = 0.29 petroleum ether/acetone 85/15 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.22-7.16 (m, 2H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 7.06 (m, 1H), 3.94 (m, 1H), 3.42-3.27 (m, 2H), 2.22 (s, 3H), 1.93-1.78 (m, 4H), 1.66 (m, 1H), 1.62-1.53 (m, 1H), 1.54-1.44 (m, 1H), 1.36 (qt, *J* = 13.0, 3.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 2H) superimposed to 1.21 (t, *J* = 7.2 Hz, 1H), 1.16-1.07 (m, 1H). $^{13}C\{^1H\}$ NMR

(150 MHz, $CDCl_3$) δ 154.3, 150.3, 131.1, 130.6, 126.9, 125.4, 122.4, 56.5, 38.3, 31.2, 26.0, 25.7, 16.5, 15.3. HRMS (ESI): *m/z* calcd for $C_{16}H_{23}NO_2 + H^+$: 262.1802 [$M+H^+$]; found 262.1807.

2-Methylphenyl-*N,N*-dicyclohexylcarbamate (1x): General procedure **C** starting from dicyclohexylamine (1.0 eq., 4.0 mmol, 0.8 mL), triethylamine (1.2 eq., 4.8 mmol, 0.67 mL) in benzene (20 mL) and triphosgene (0.34 eq., 1.36 mmol, 0.40 g) gave *N,N*-dicyclohexylcarbamoylchloride as yellow solid (0.78 g, 80%), which was used without any further purification. To a stirred solution of *N,N*-dicyclohexylcarbamoilchloride (1 eq., 2.88 mmol, 0.70 g) in anhydrous pyridine, *ortho*-cresol (1.0 eq., 2.88 mmol, 0.30 mL) was added. Purification by flash column chromatography on silica gel (petroleum ether/Et_2O 95/5 v/v) gave **1x** as a white solid (0.50 g, 55%, R_f = 0.18 petroleum ether/Et_2O 95/5 v/v), mp. 102.5-103.8 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 7.10 (td, *J* = 7.5, 1.3 Hz, 1H), 7.04 (dd, *J* = 8.0, 0.9 Hz, 1H), 3.59 (br s, 2H), 2.22 (s, 3H), 1.96-1.75 (m, 10H) superimposed to 1.67 (m, 4H), 1.34 (t, *J* = 11.5 Hz, 4H), 1.13 (qt, *J* = 13.1, 3.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 153.8, 150.2, 131.0, 130.8, 126.8, 125.3, 122.4, 56.0, 31.8, 30.7, 26.5, 26.3, 25.5, 16.6. HRMS (ESI): *m/z* calcd for $C_{20}H_{29}NO_2 + H^+$: 316.2271 [$M+H^+$]; found 316.2275.

2-Methylphenyl pyrrolidine-1-carboxylate (1y): General procedure **A** starting from *ortho*-cresol (1.0 eq., 3.0 mmol, 0.31 mL) and 1-pyrrolidinecarbamoyl chloride (1.0 eq., 3.0 mmol, 0.33 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 8/2 v/v) gave **1y** as a yellow oil (0.35 g, 57%, R_f = 0.16 petroleum ether/Et_2O 8/2 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.22-7.16 (m, 2H), 7.10 (ddd, *J* = 8.2, 5.7, 1.5 Hz, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 2.23 (s, 3H), 2.04-1.88 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.1, 150.1, 131.0, 130.5, 126.9, 125.4, 122.4, 46.6, 46.5, 26.0, 25.2, 16.4. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}NO_2 + H^+$: 206.1176 [$M+H^+$]; found 206.1180.

2-Methylphenyl piperidine-1-carboxylate (1z): According to general procedure **B** in THF starting from piperidine (1.0 eq., 5.0 mmol, 0.5 mL), using CDI (1.1 eq., 5.5 mmol, 0.89 g), iodomethane (4.0 eq., 16.0 mmol, 1.0 mL), *ortho*-cresol (1.0 eq., 3.82 mmol, 0.39 mL) and triethylamine (1.0 eq., 3.82 mmol, 0.53 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 8/2 v/v) gave **1z** as a yellow oil (0.66 g, 60%, R_f = 0.31 petroleum ether/Et_2O 8/2 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.22-7.17 (m, 2H), 7.10 (td, *J* = 7.4, 1.3 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.64 (s, 2H), 3.52 (s, 2H), 2.21 (s, 3H), 1.71-1.60 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 153.6, 150.2, 131.0, 130.5, 126.9, 125.5, 122.4, 45.7, 45.3, 26.2, 25.7, 24.5, 16.3. HRMS (ESI): *m/z* calcd for $C_{13}H_{17}NO_2 + H^+$: 220.1332 [$M+H^+$]; found 220.1337.

2-Methylphenylmorpholine-4-carboxylate (1aa): According to general procedure **B** in DCM starting from morpholine (1.0 eq., 20.0 mmol, 1.7 mL), CDI (1.1 eq., 22.0 mmol, 3.6 g), iodomethane (4.0 eq., 68.0 mmol, 4.2 mL), *ortho*-cresol (1.0 eq., 10.0 mmol, 1.0 mL) and triethylamine (1.0 eq., 10.0 mmol, 1.4 mL); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 8/2 v/v) gave **1aa** as a yellow oil (1.90 g, 43%, R_f = 0.30 petroleum ether/EtOAc 8/2 v/v). ^1H NMR (600 MHz, $CDCl_3$) δ 7.23-7.18 (m, 2H), 7.12 (td, *J* = 7.5, 1.3 Hz, 1H), 7.06 (dd, *J* = 7.9, 1.2 Hz, 1H), 3.77-3.74 (m, 4H), 3.71 (br s, 2H), 3.58 (br s, 2H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 153.6, 149.8, 131.2, 130.4, 127.0, 125.8, 122.3, 66.9, 66.8, 45.1,

44.3, 16.2. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}NO_3 + H^+$: 222.1125 [M+H$^+$]; found 222.1129. All analytical data were in good accordance with those reported in the literature.[9]

2-Methylphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (1ab): According to general procedure **B** in THF starting from 1,2,3,4-tetrahydroquinoline (1.0 eq., 15.0 mmol, 1.9 mL), using CDI (1.1 eq., 16.0 mmol, 2.68 g), iodomethane (4.0 eq., 59.0 mmol, 3.7 mL), *ortho*-cresol (1.0 eq., 14.35 mmol, 1.5 mL) and triethylamine (1.0 eq., 14.35 mmol, 2.0 mL); purification by flash column chromatography on silica gel (petroleum ether/acetone 95/15 v/v) gave **1ab** as a white solid (3.14 g, 79%, R_f = 0.40 petroleum ether/acetone 95/5 v/v), mp. 72.8-74.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (br s, 1H), 7.25-7.20 (m, 2H), 7.18 (m, 1H), 7.16-7.11 (m, 3H), 7.05 (td, *J* = 7.4, 1.2 Hz, 1H), 3.96 (t, *J* = 6.1 Hz, 2H), 2.86 (t, *J* = 6.6 Hz, 2H), 2.25 (s, 3H), 2.05 (quint, *J* = 6.5 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.1, 149.9, 138.1, 131.2, 130.5, 128.7, 127.0, 126.3, 125.9, 124.2, 122.3, 45.5, 27.5, 23.7, 16.5. HRMS (ESI): *m/z* calcd for $C_{17}H_{17}NO_2 + H^+$: 268.1332 [M+H$^+$]; found 268.1337.

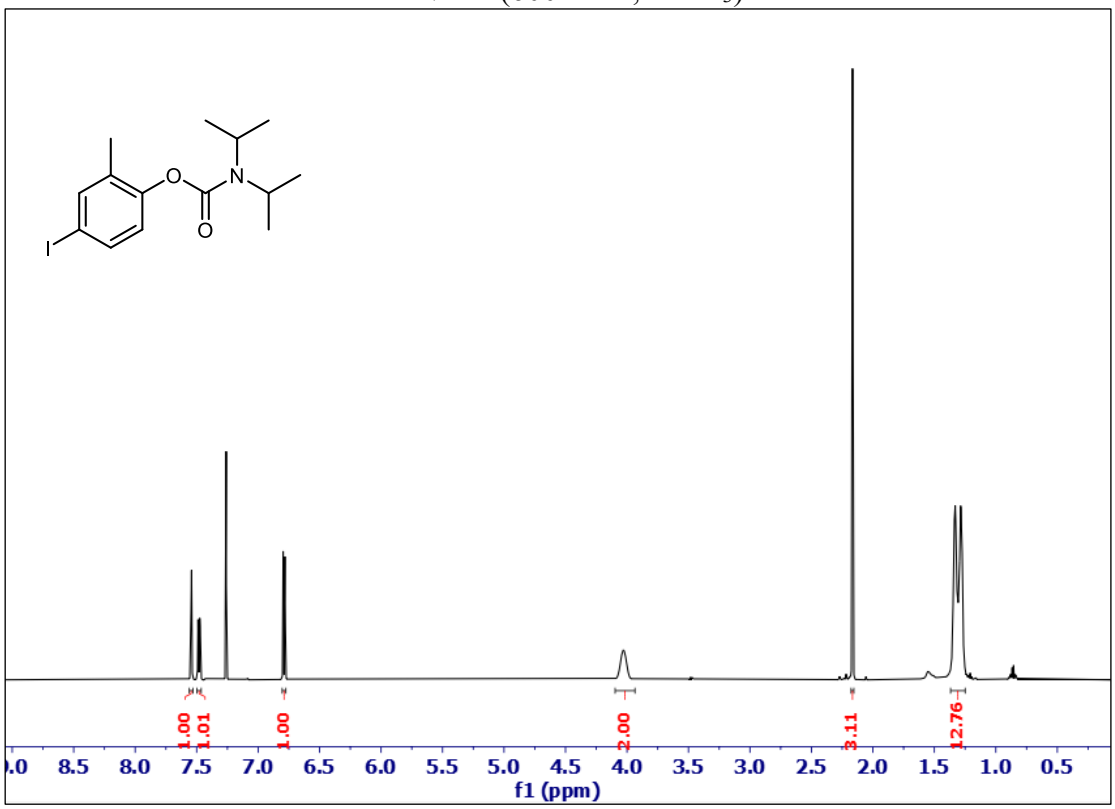
2-Methylphenyl-*N*-phenyl-*N*'-methylcarbamate (1ac): According to general procedure **B** in THF starting from *N*-methylaniline (1.0 eq., 15.0 mmol, 1.62 mL), using CDI (1.1 eq., 1.65 mmol, 2.68 g), iodomethane (4.0 eq., 48.0 mmol, 3.0 mL), *ortho*-cresol (1.0 eq., 12.0 mmol, 1.3 mL) and triethylamine (1.0 eq., 12.0 mmol, 1.7 mL); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 9/1 v/v) gave **1ac** as a yellow oil (2.22 g, 62%, R_f = 0.24 petroleum ether/Et_2O 9/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43-7.37 (m, 4H), 7.30-7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 2H), 3.44 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 153.8, 150.0, 143.2, 131.1, 130.4, 129.2, 126.9, 125.7, 122.2, 38.4, 16.4. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}NO_2 + H^+$: 242.1176 [M+H$^+$]; found 242.1180.

2-Methylphenyl-*N*,*N*-diphenylcarbamate (1ad): General procedure **A** starting from *ortho*-cresol (1.0 eq., 3.0 mmol, 0.31 mL) and *N*,*N*-diphenylcarbamoyl chloride (1.0 eq., 3.0 mmol, 0.70 g); purification by flash column chromatography on silica gel (petroleum ether/Et_2O 98/2 v/v) gave **1ad** as a colourless oil (0.73 g, 81%, R_f = 0.13 petroleum ether/Et_2O 98/2 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.35 (m, 8H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 2H), 7.15 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.10 (td, *J* = 7.3, 1.6 Hz, 1H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.9, 149.9, 142.4, 131.1, 130.3, 129.2, 126.9, 126.6, 125.8, 122.0, 16.5. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}NO_2 + H^+$: 304.1332 [M+H$^+$]; found 304.1338.

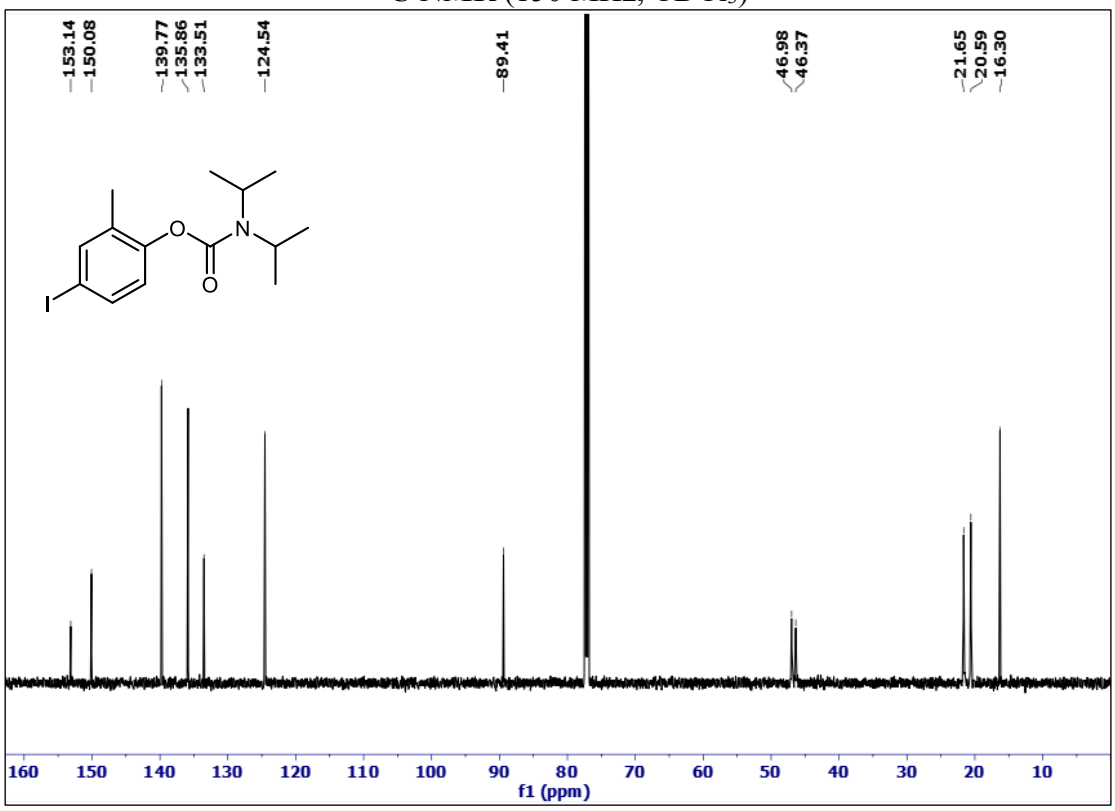
^{1}H and ^{13}C NMR spectra of carbamates **1**

2-Methyl-4-iodophenyl *N*,*N*-diisopropylcarbamate (1d)

^{1}H NMR (600 MHz, $CDCl_3$)

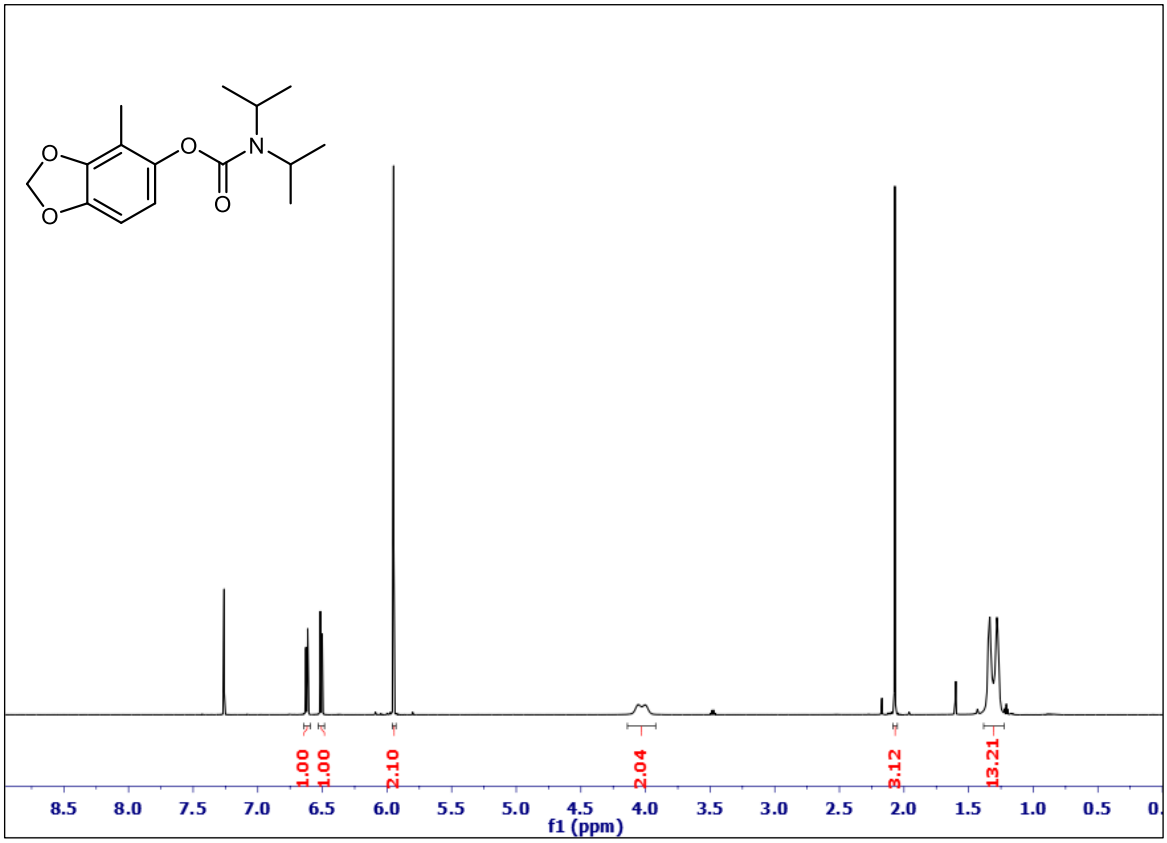


^{13}C NMR (150 MHz, $CDCl_3$)

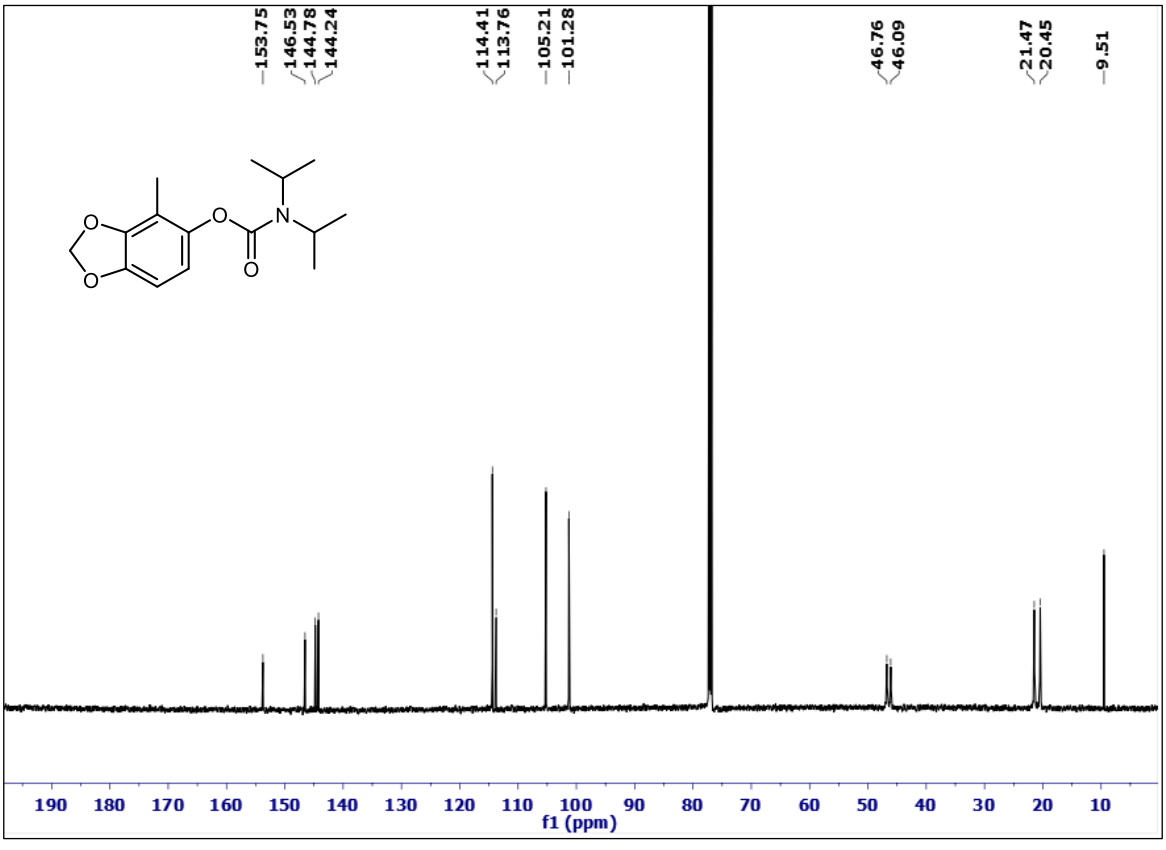


4-Methylbenzo[d][1,3]dioxol-5-yl-*N*,*N*-diisopropylcarbamate (1i)

^{1}H NMR (600MHz, $CDCl_3$)

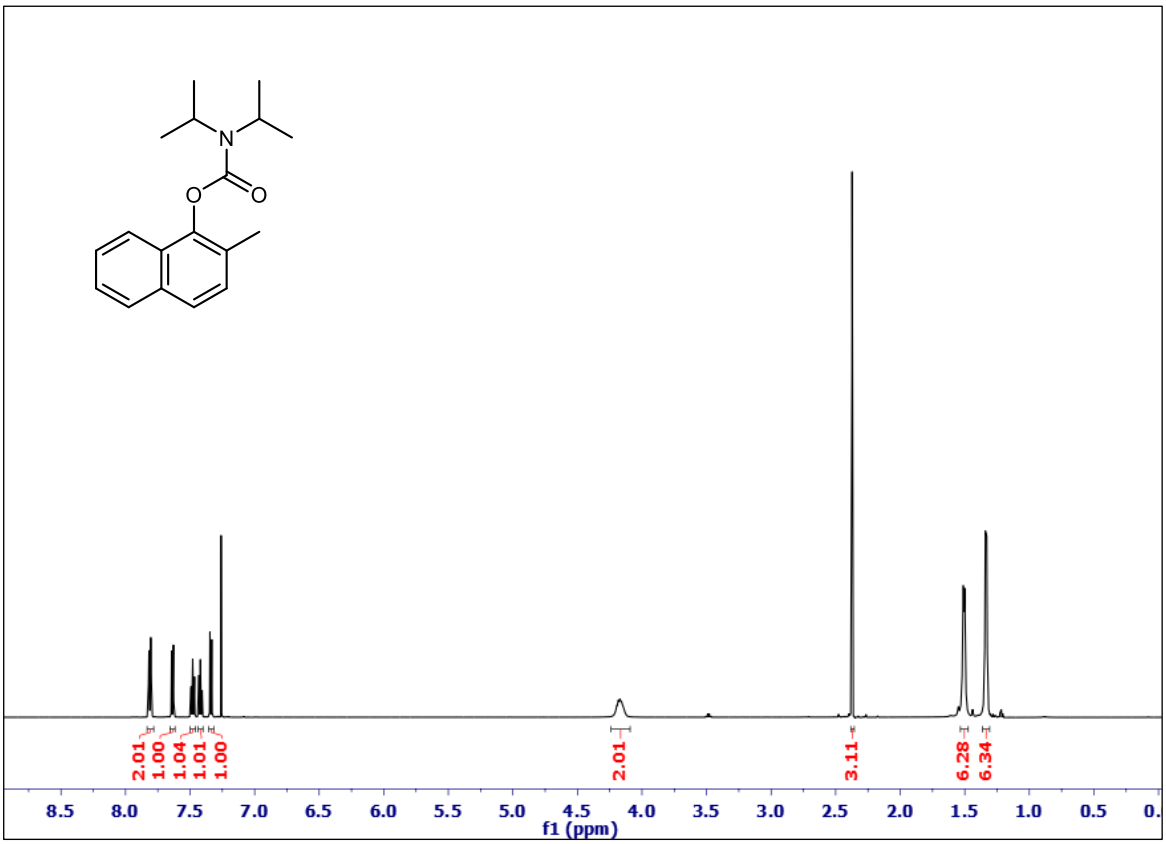


^{13}C NMR (150 MHz, $CDCl_3$)

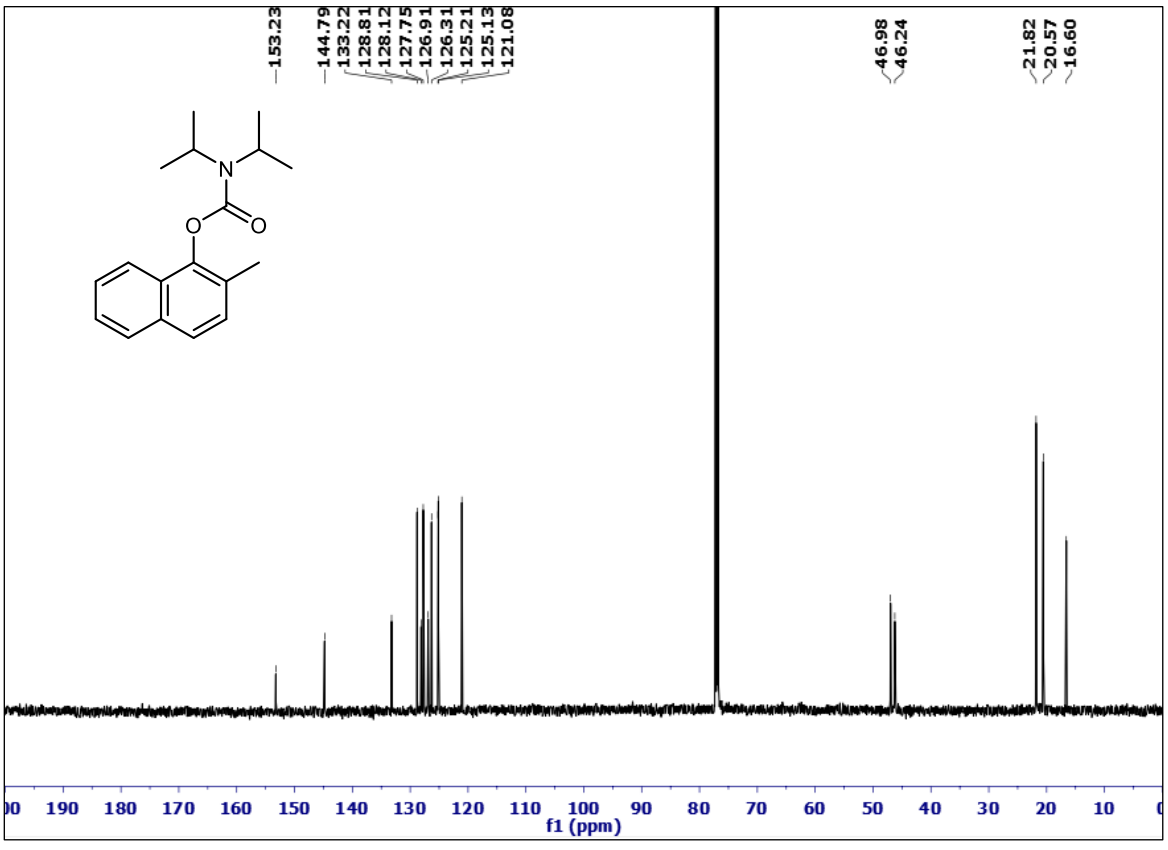


2-Methylnaphtalen-1-yl-*N*,*N*-diisopropylcarbamate (1k)

^{1}H NMR (600 MHz, $CDCl_3$)

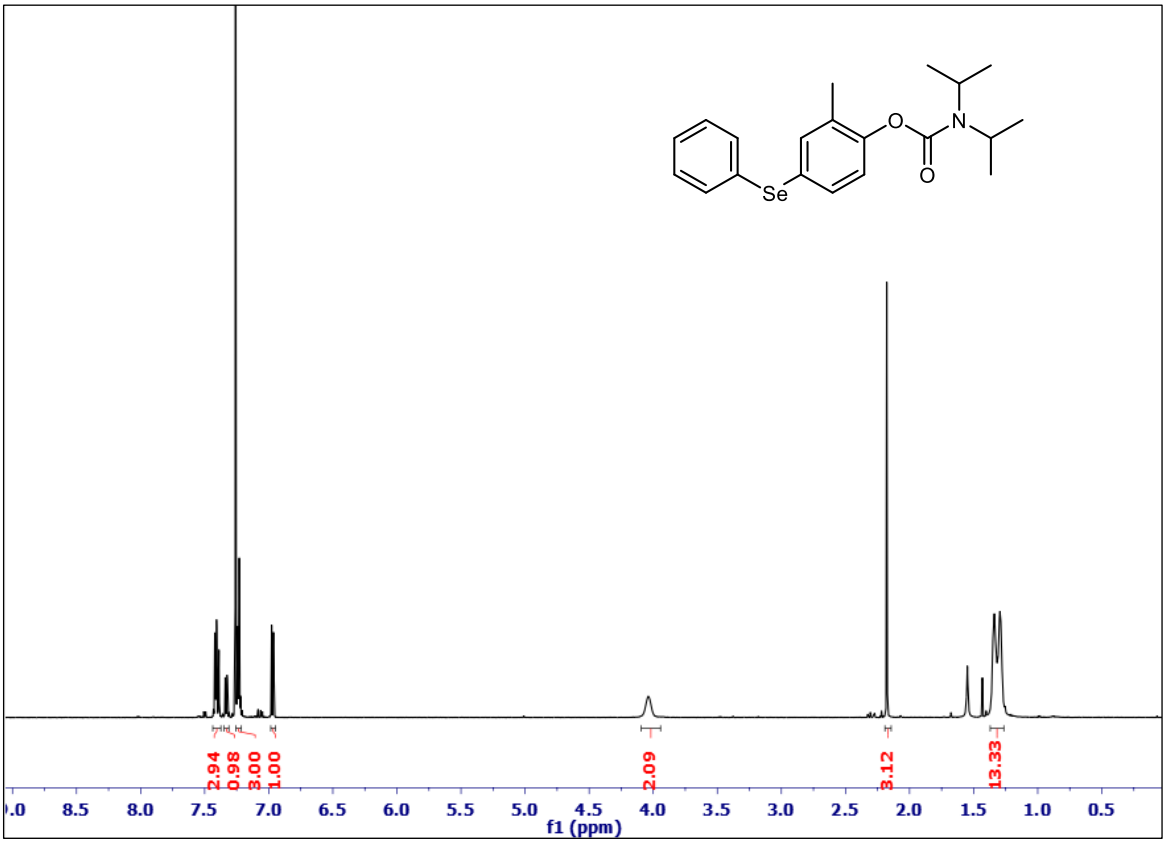


^{13}C NMR (150 MHz, $CDCl_3$)

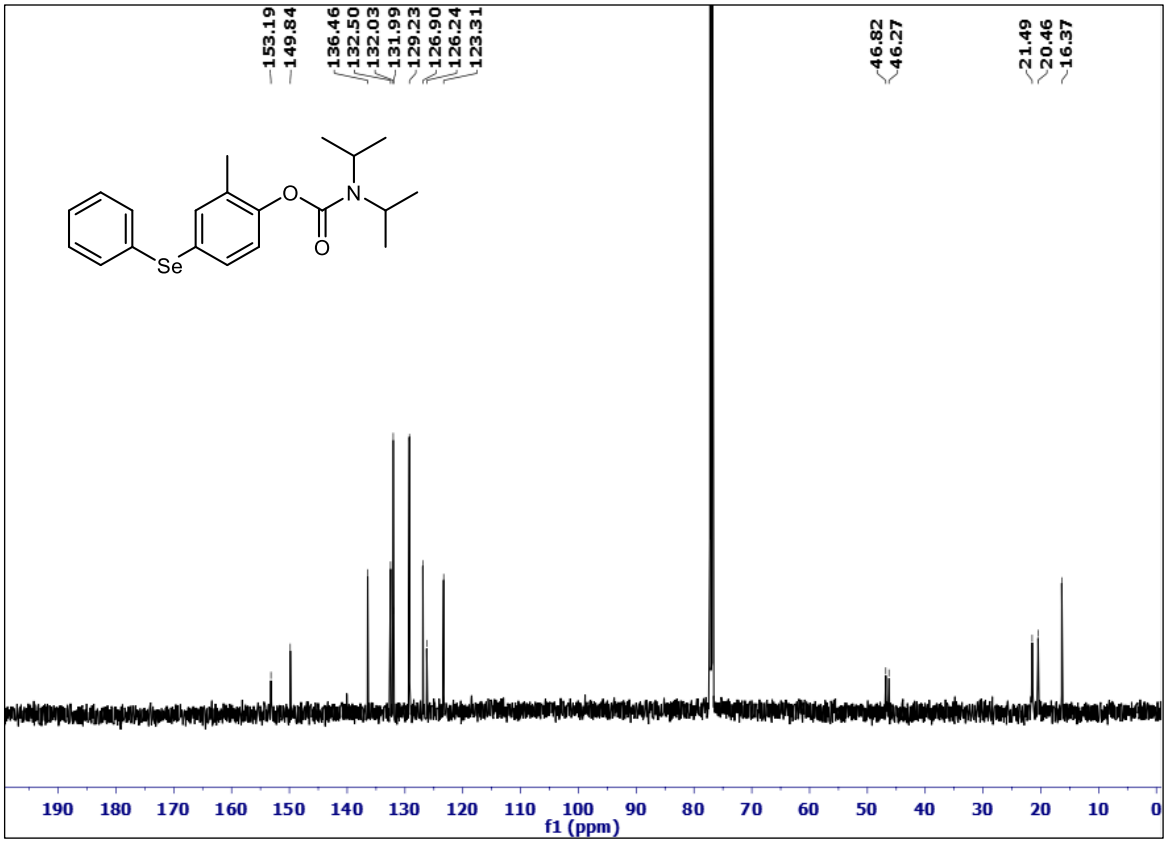


2-Methyl-4-(phenylselanyl)phenyl-*N*,*N*-diisopropylcarbamate (1l)

^{1}H NMR (600 MHz, $CDCl_3$)

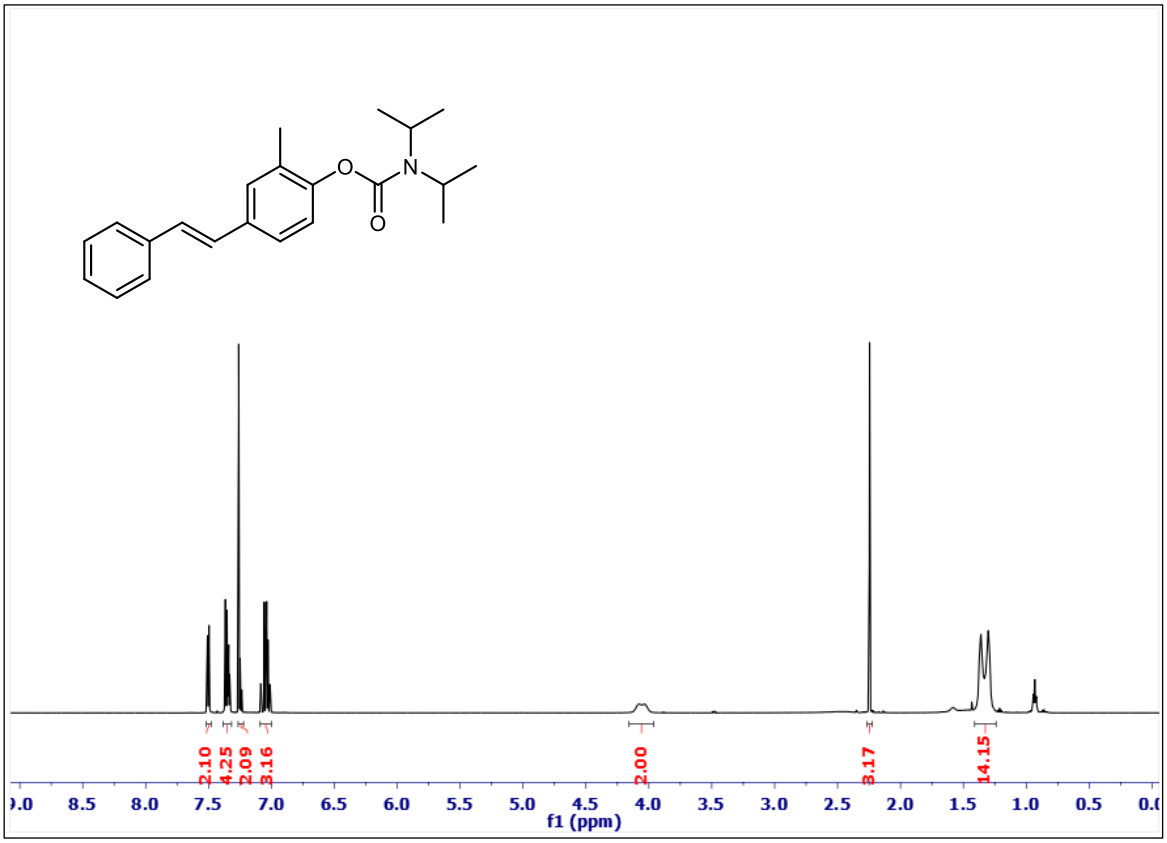


^{13}C NMR (150 MHz, $CDCl_3$)

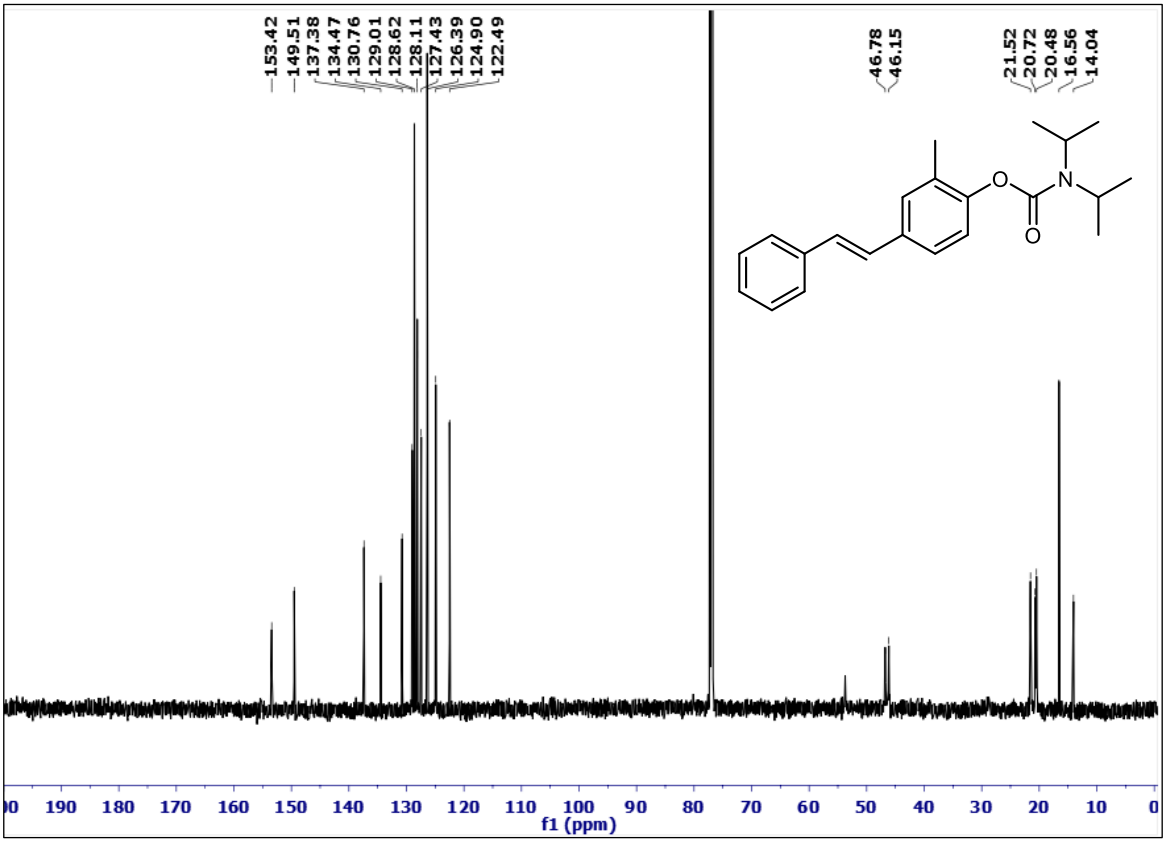


2-Methyl-4-styrylphenyl-*N*,*N*-diisopropylcarbamate (1m)

^{1}H NMR (600 MHz, $CDCl_3$)

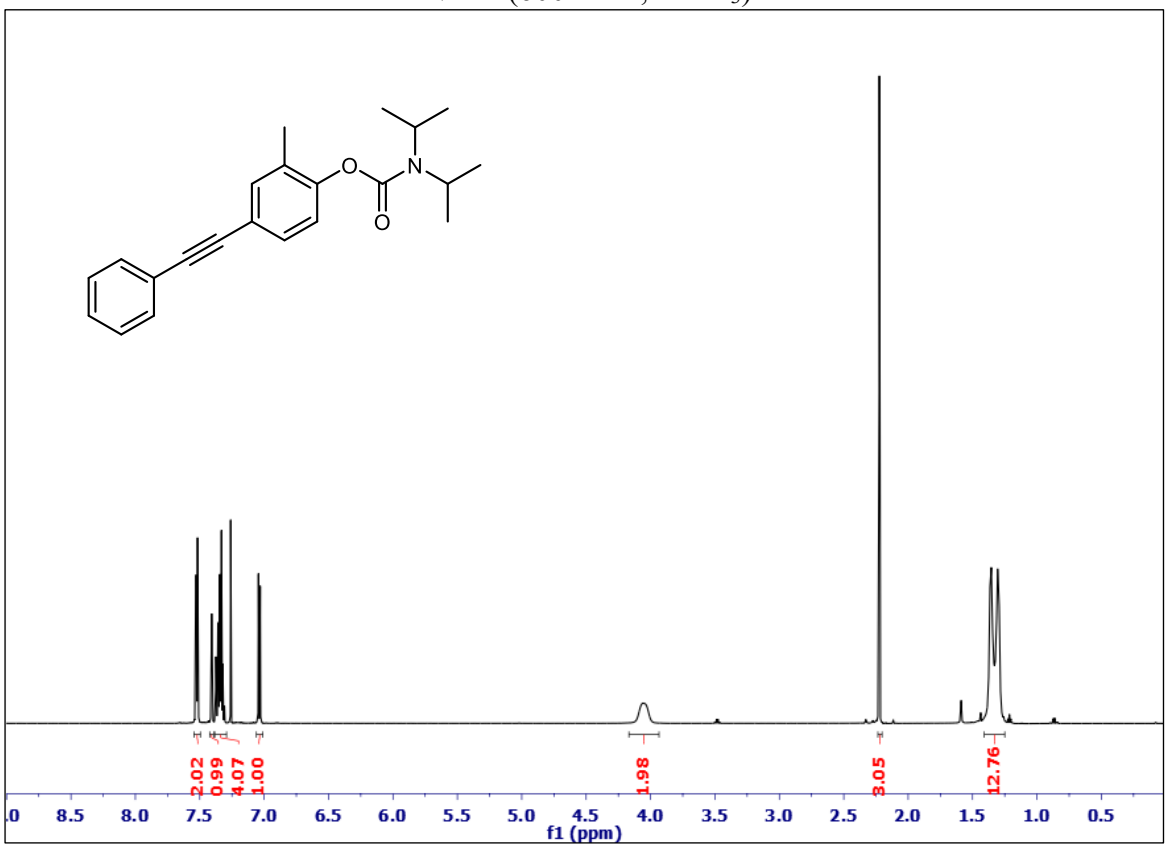


^{13}C NMR (150 MHz, $CDCl_3$)

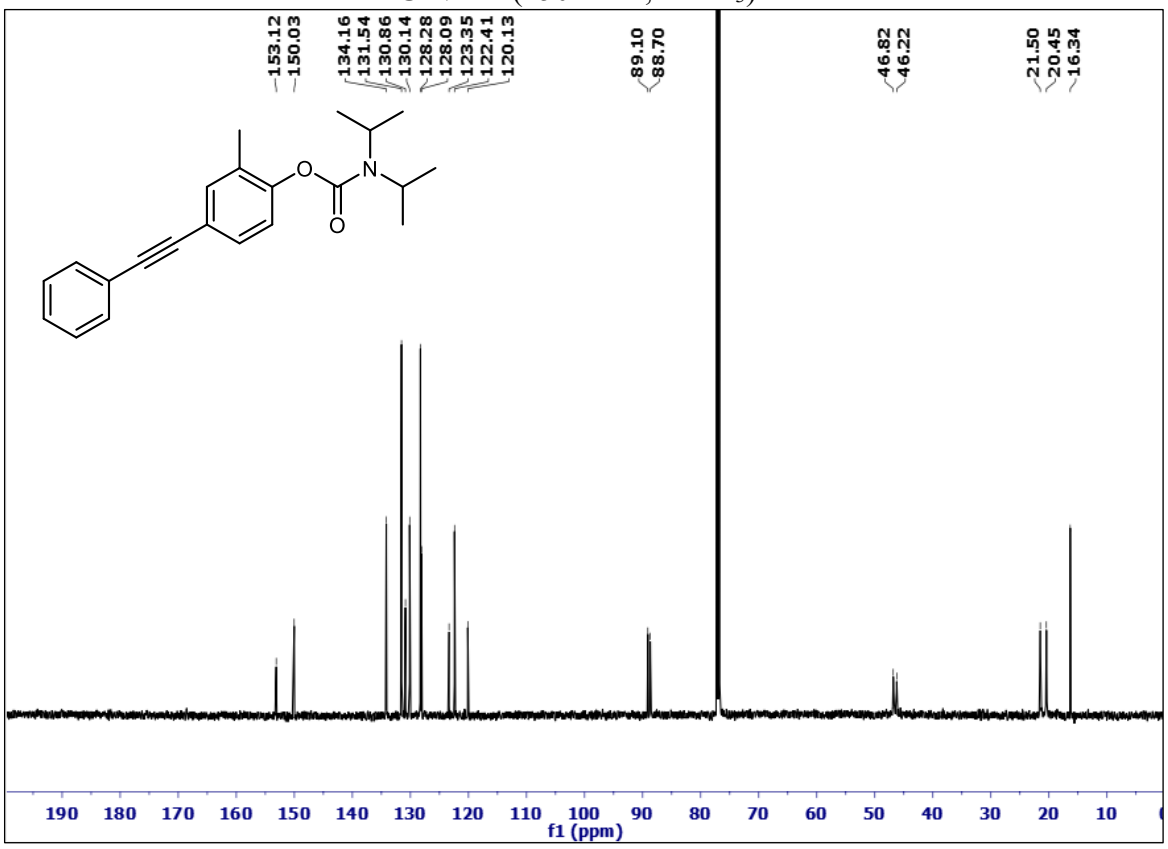


2-Methyl-4-(phenylethynyl)phenyl-*N*,*N*-diisopropylcarbamate (1n)

^{1}H NMR (600 MHz, $CDCl_3$)

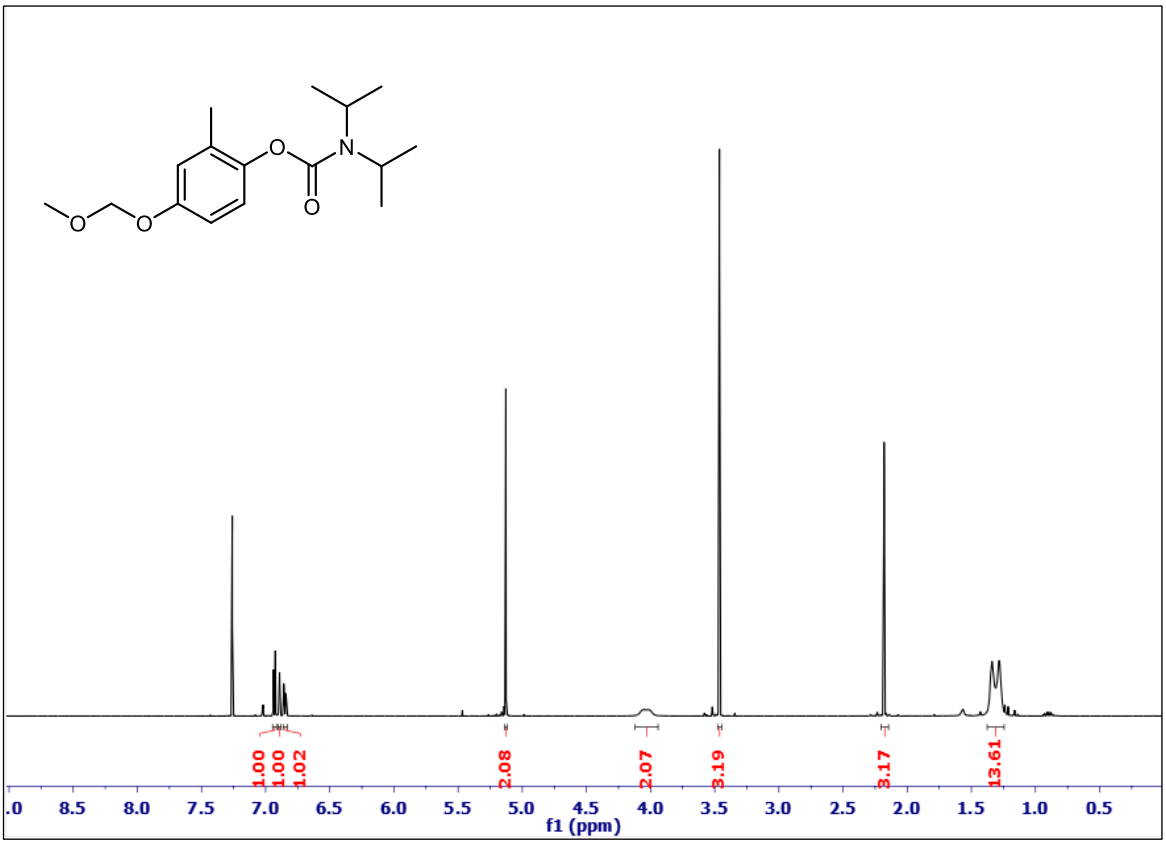


^{13}C NMR (150 MHz, $CDCl_3$)

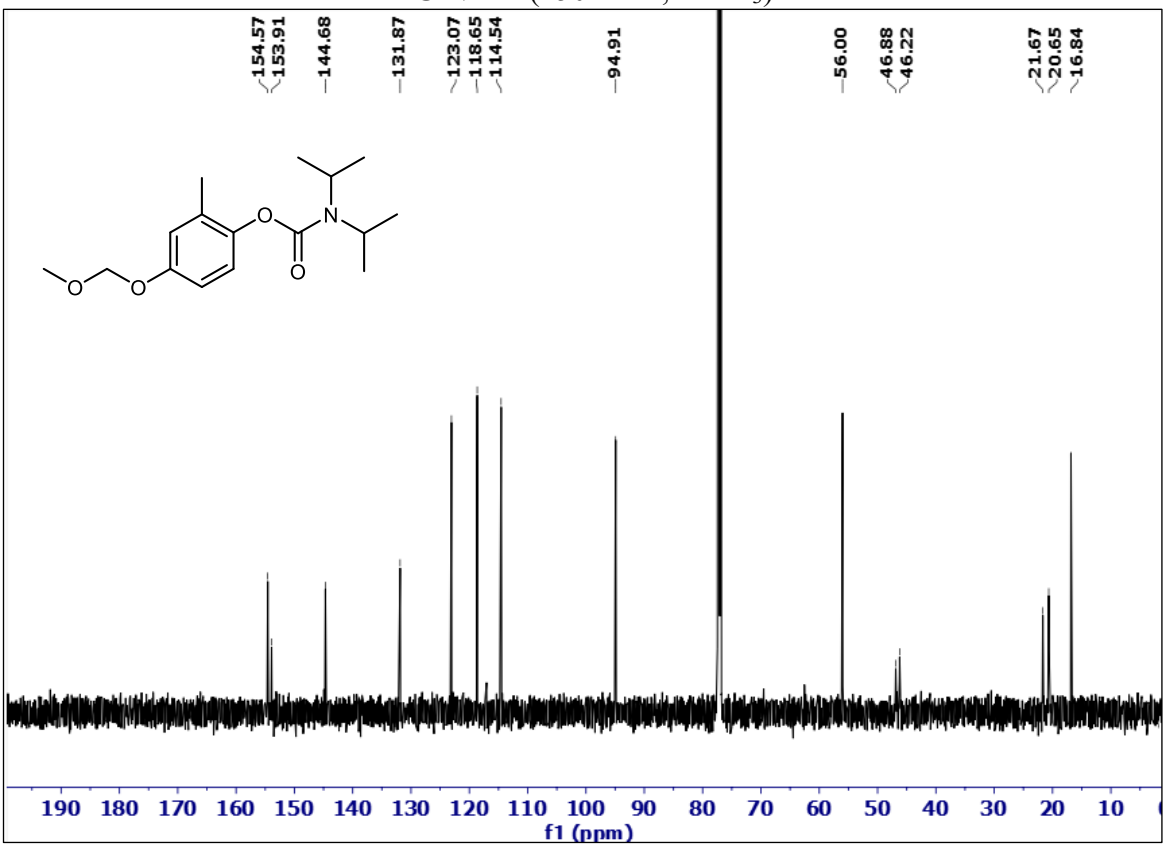


4-(Methoxymethoxy)-2-methylphenyl-*N*,*N*-diisopropylcarbamate (1o)

^{1}H NMR (600MHz, $CDCl_3$)

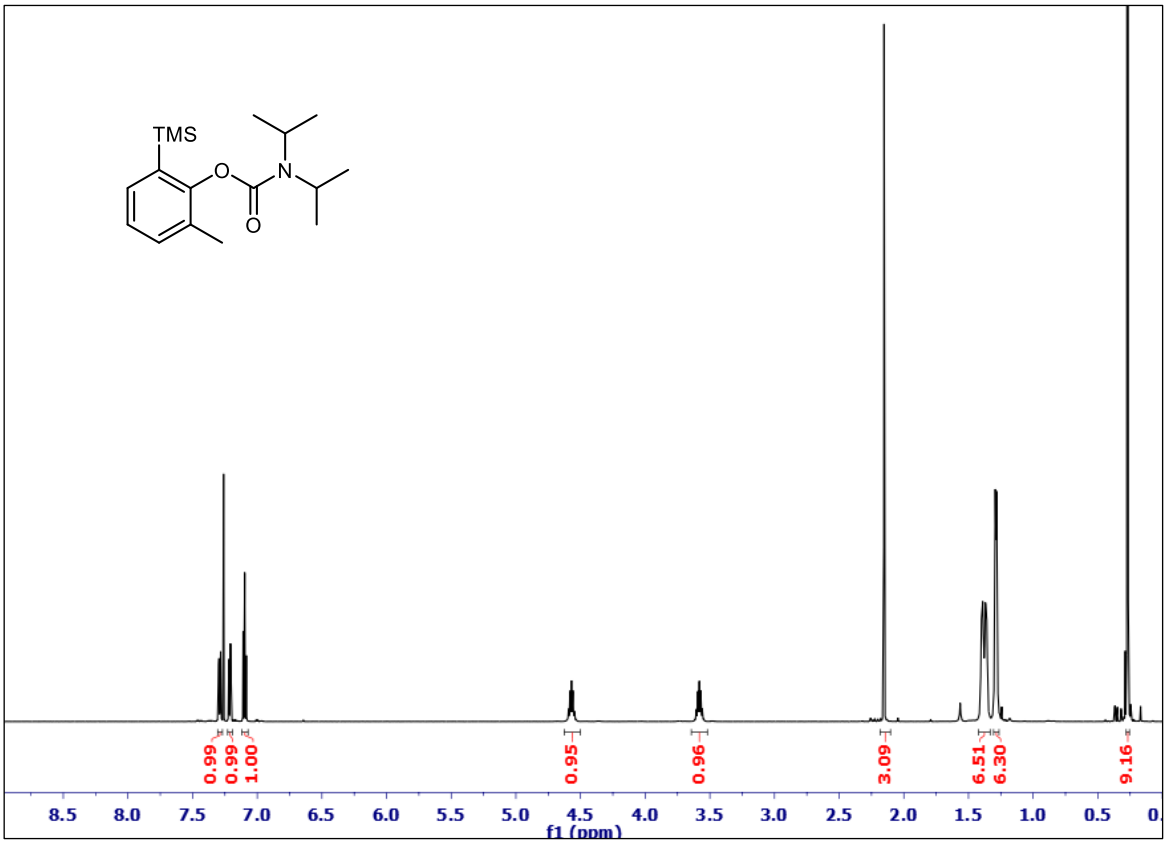


^{13}C NMR (150 MHz, $CDCl_3$)

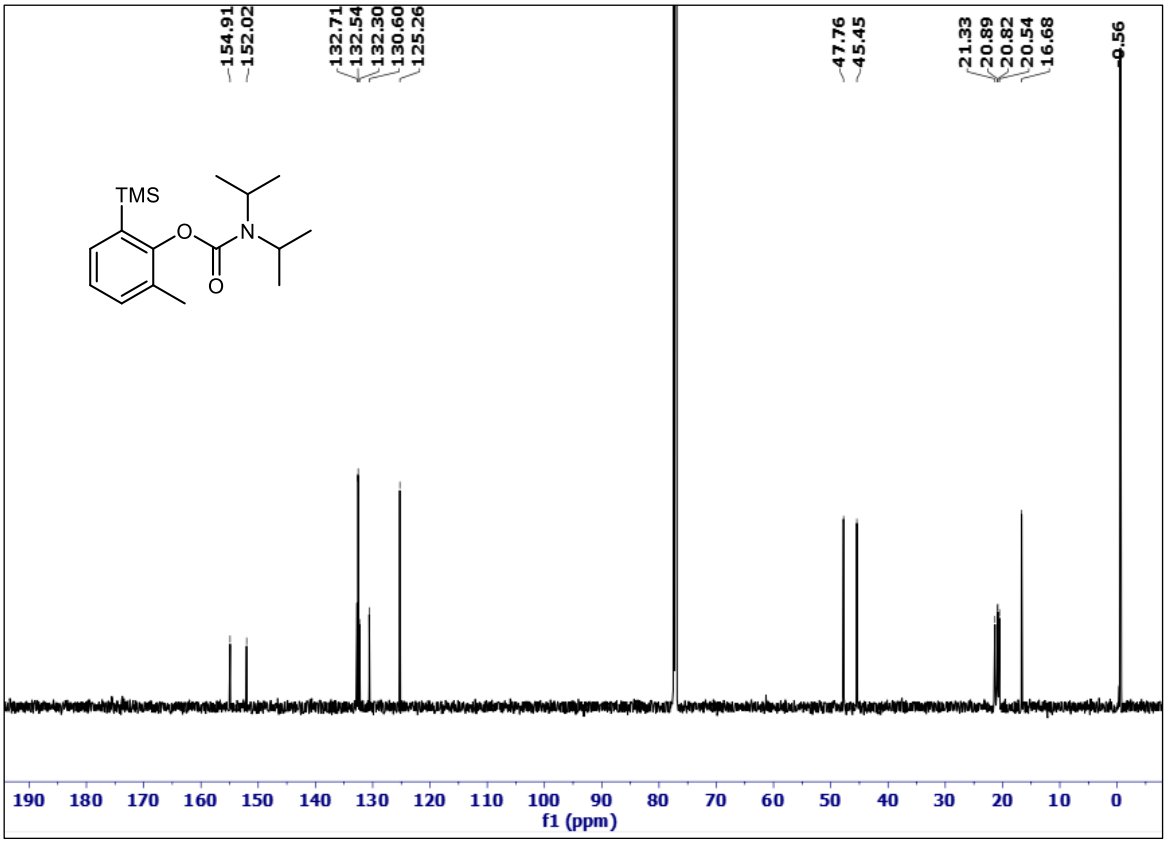


2-Methyl-6-(trimethylsilyl)phenyl-*N*,*N*-diisopropylcarbamate (1p)

^{1}H NMR (600 MHz, $CDCl_3$)

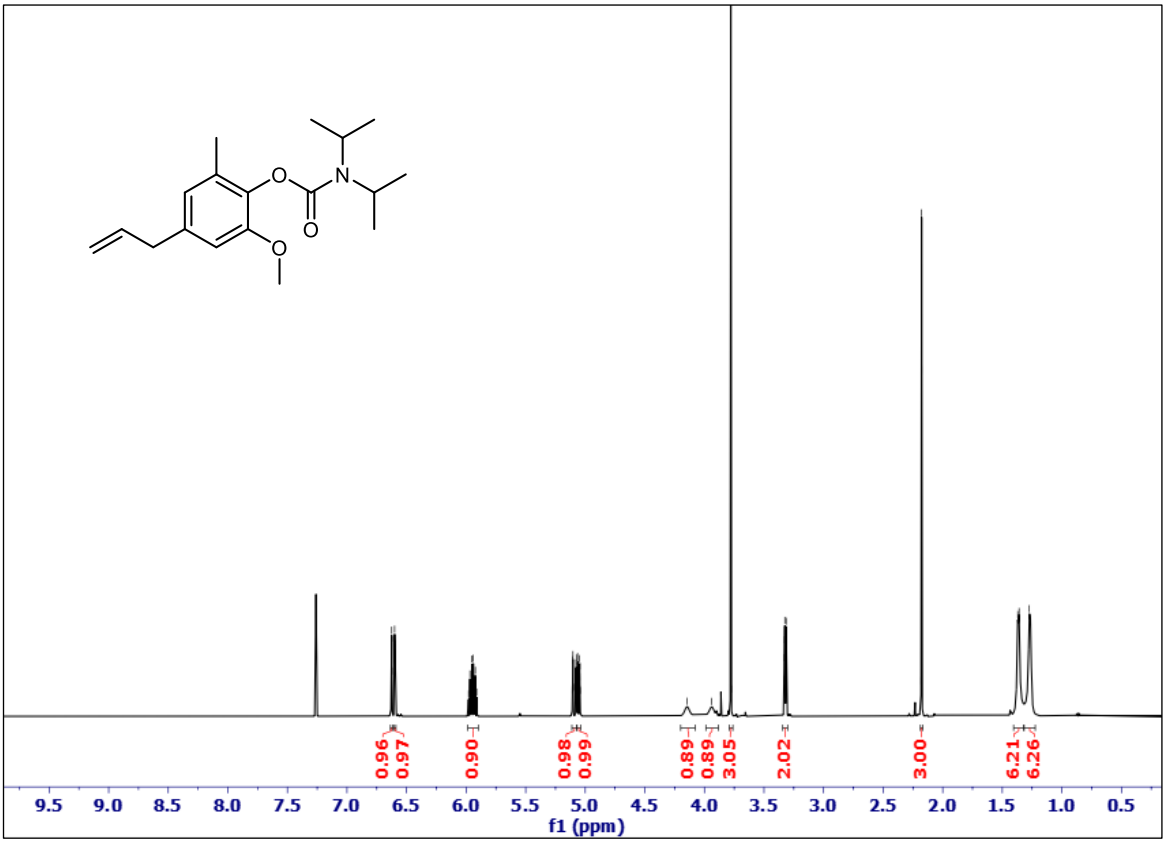


^{13}C NMR (150 MHz, $CDCl_3$)

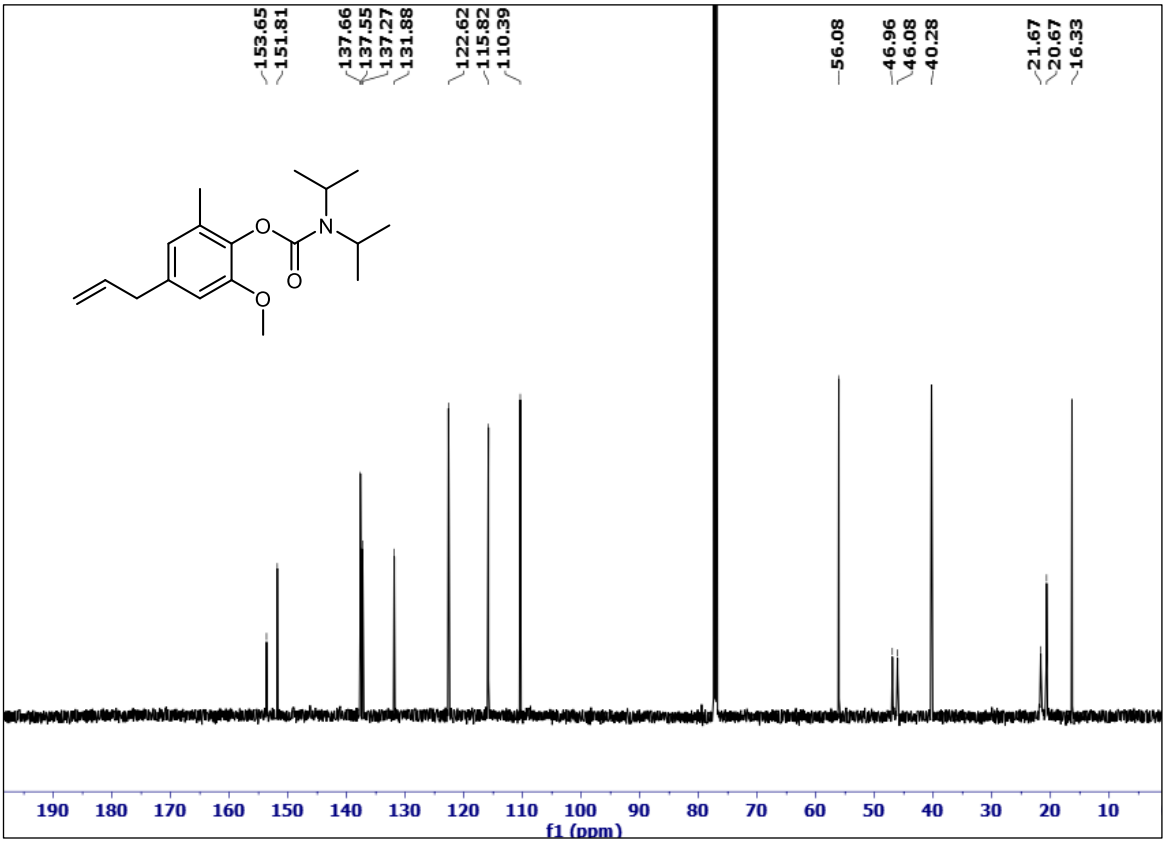


4-Allyl-2-methoxy-6-methylphenyl-*N*,*N*-diisopropylcarbamate (1q)

^{1}H NMR (600 MHz, $CDCl_3$)

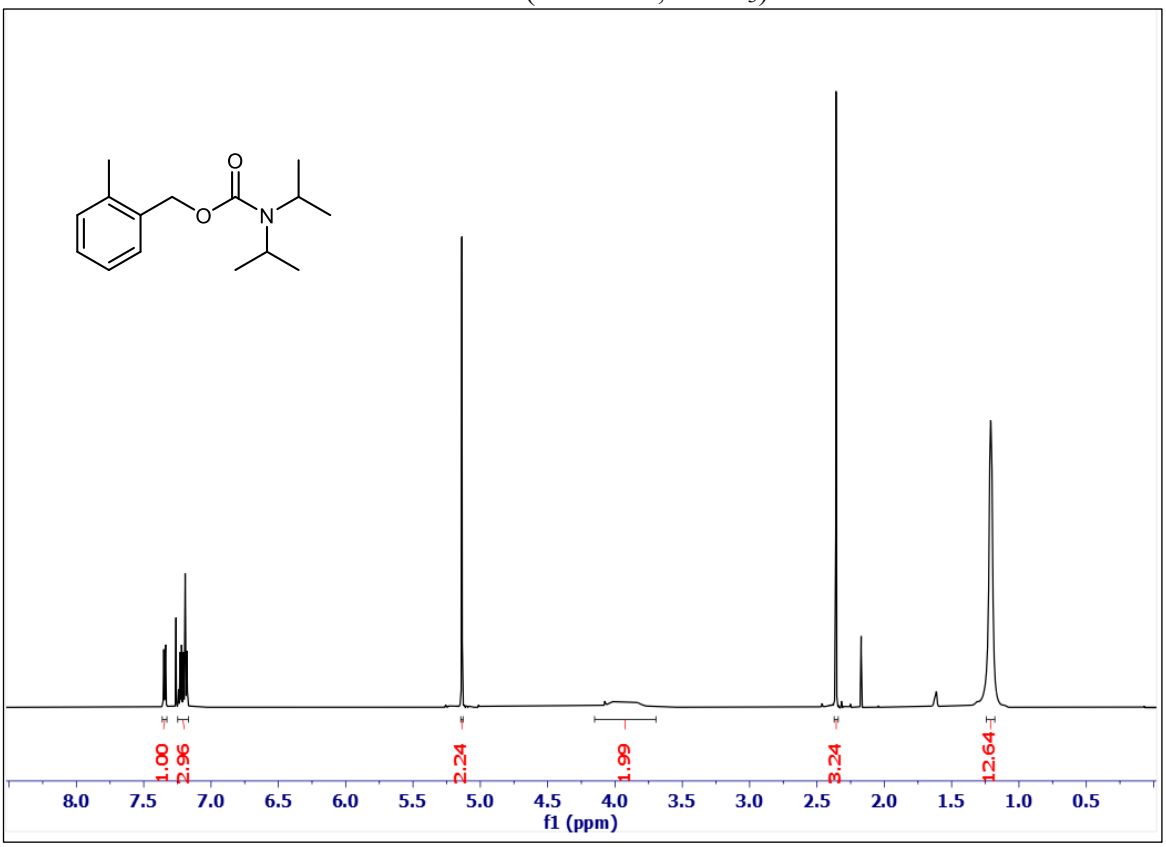


^{13}C NMR (150 MHz, $CDCl_3$)

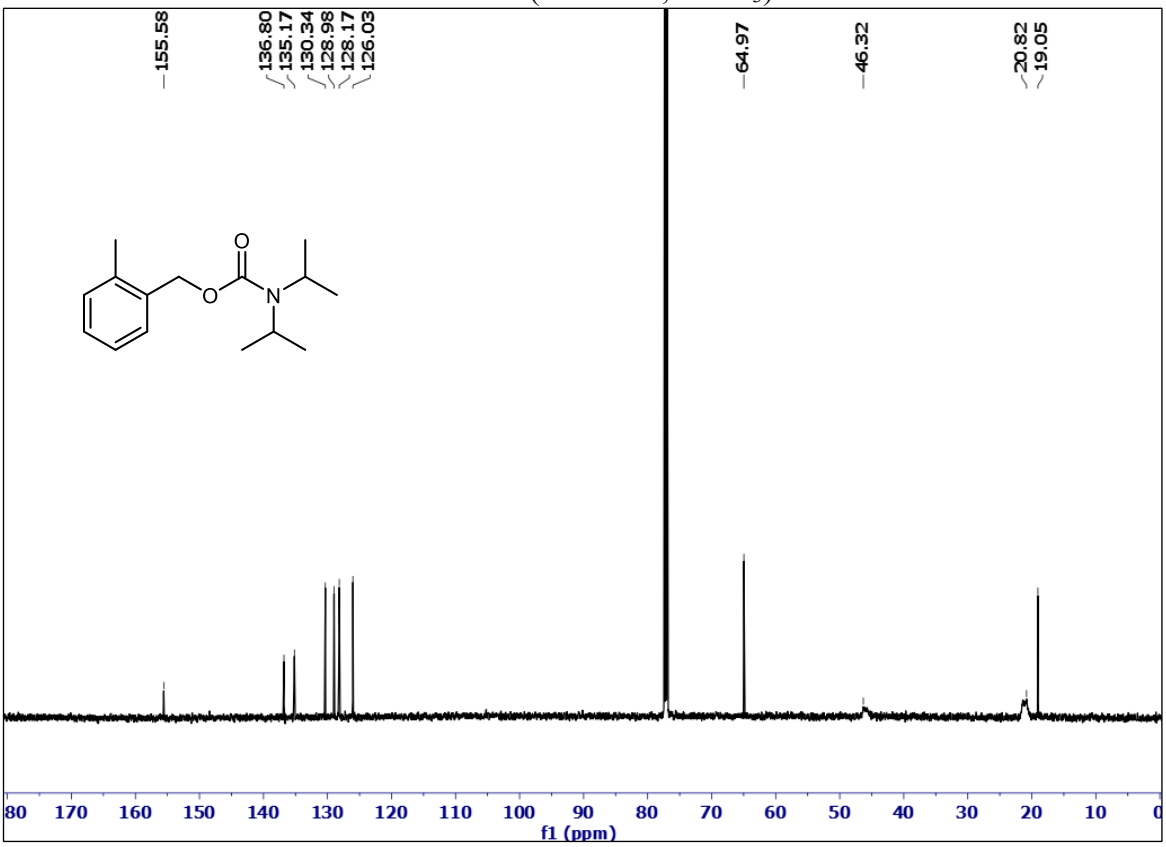


2-Methylbenzyl *N*,*N*-diisopropylcarbamate (1r)

^{1}H NMR (600 MHz, $CDCl_3$)

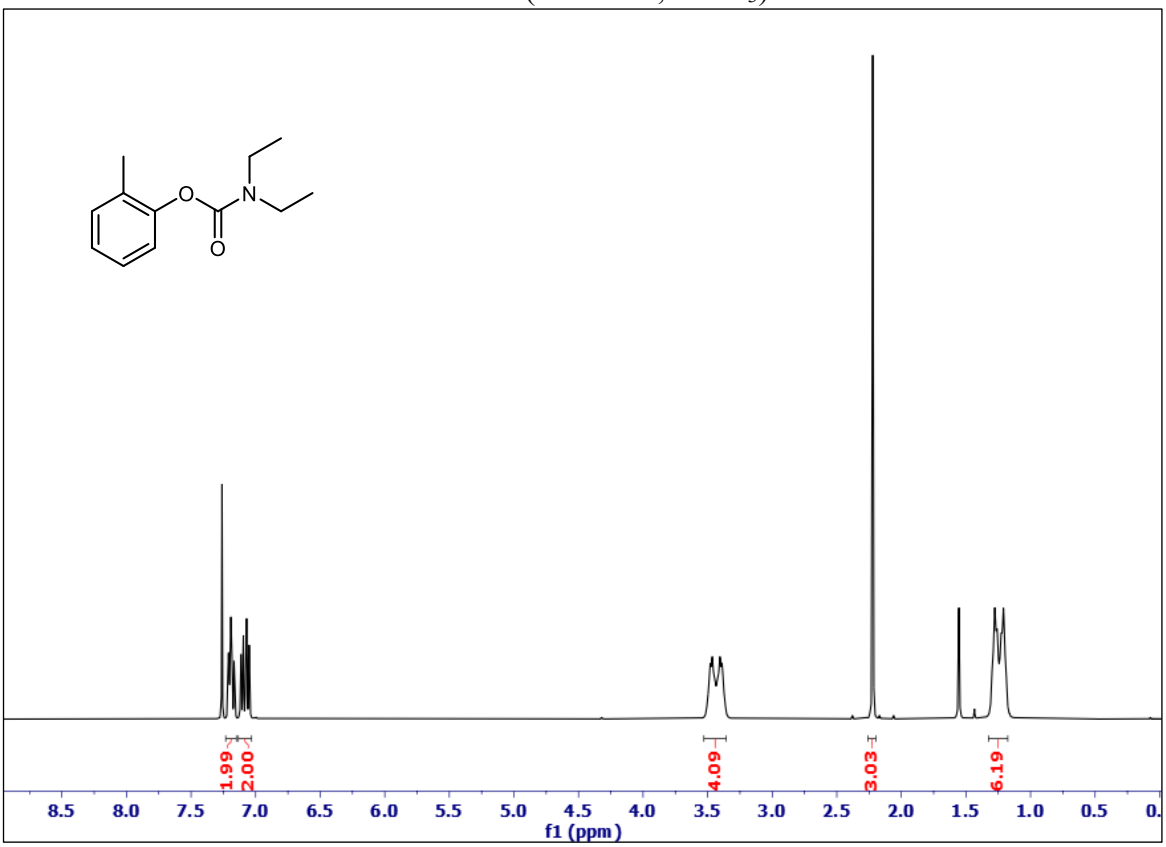


^{13}C NMR (100 MHz, $CDCl_3$)

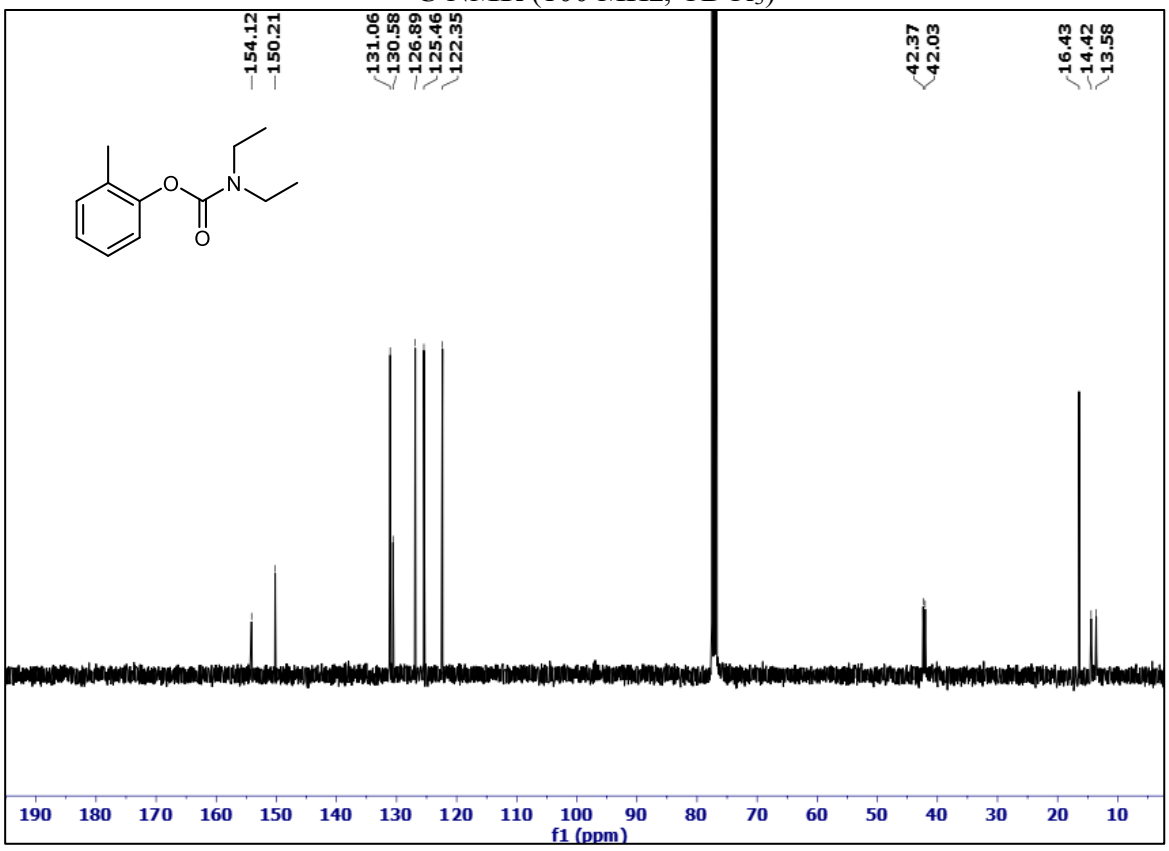


2-Methylphenyl-*N*,*N*-diethylcarbamate (1s)

^{1}H NMR (400 MHz, $CDCl_3$)

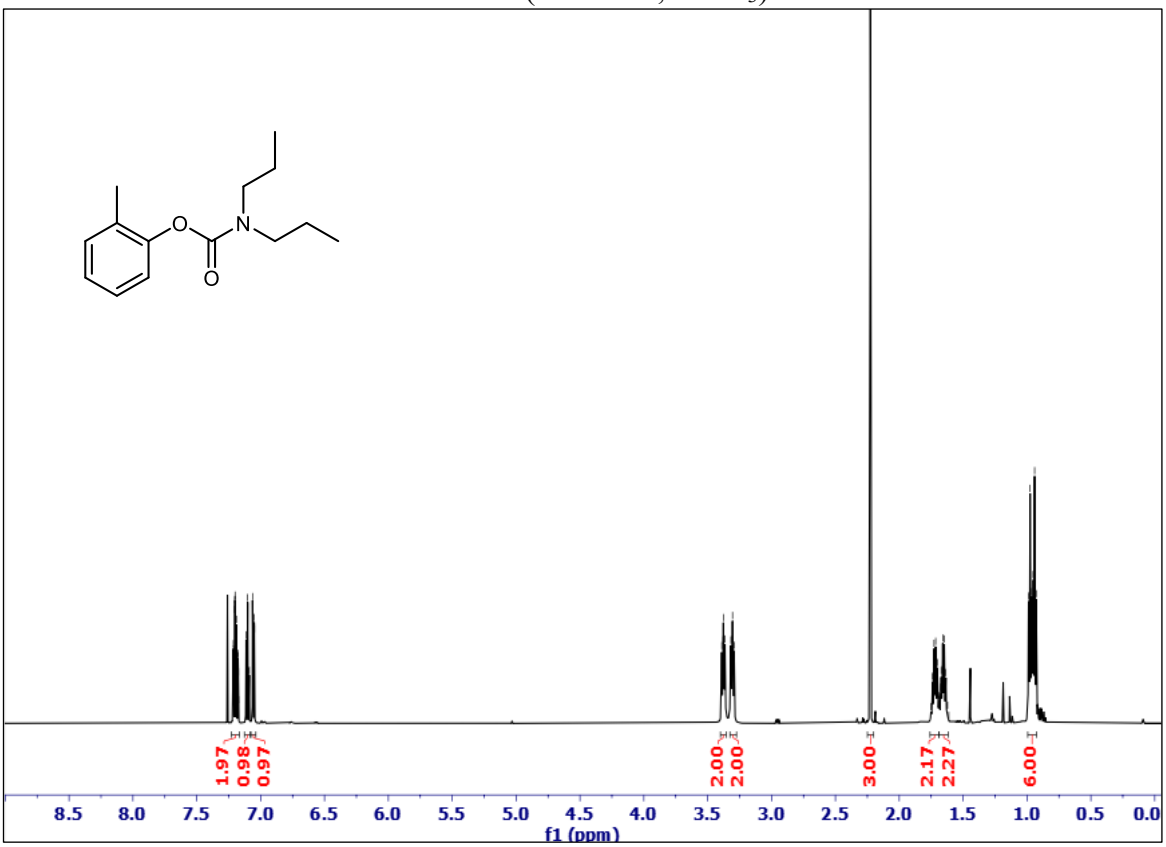


^{13}C NMR (100 MHz, $CDCl_3$)

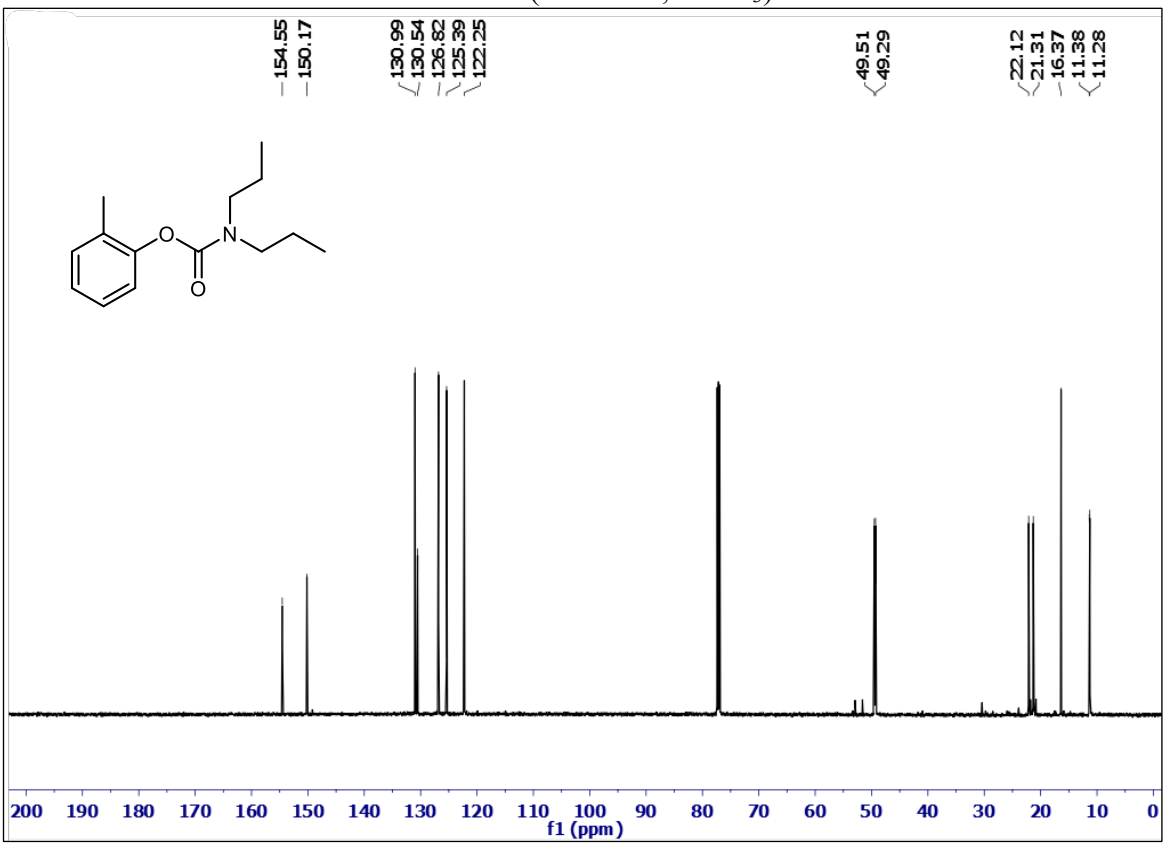


2-Methylphenyl-*N*,*N*-dipropylcarbamate (1t)

^{1}H NMR (600 MHz, $CDCl_3$)

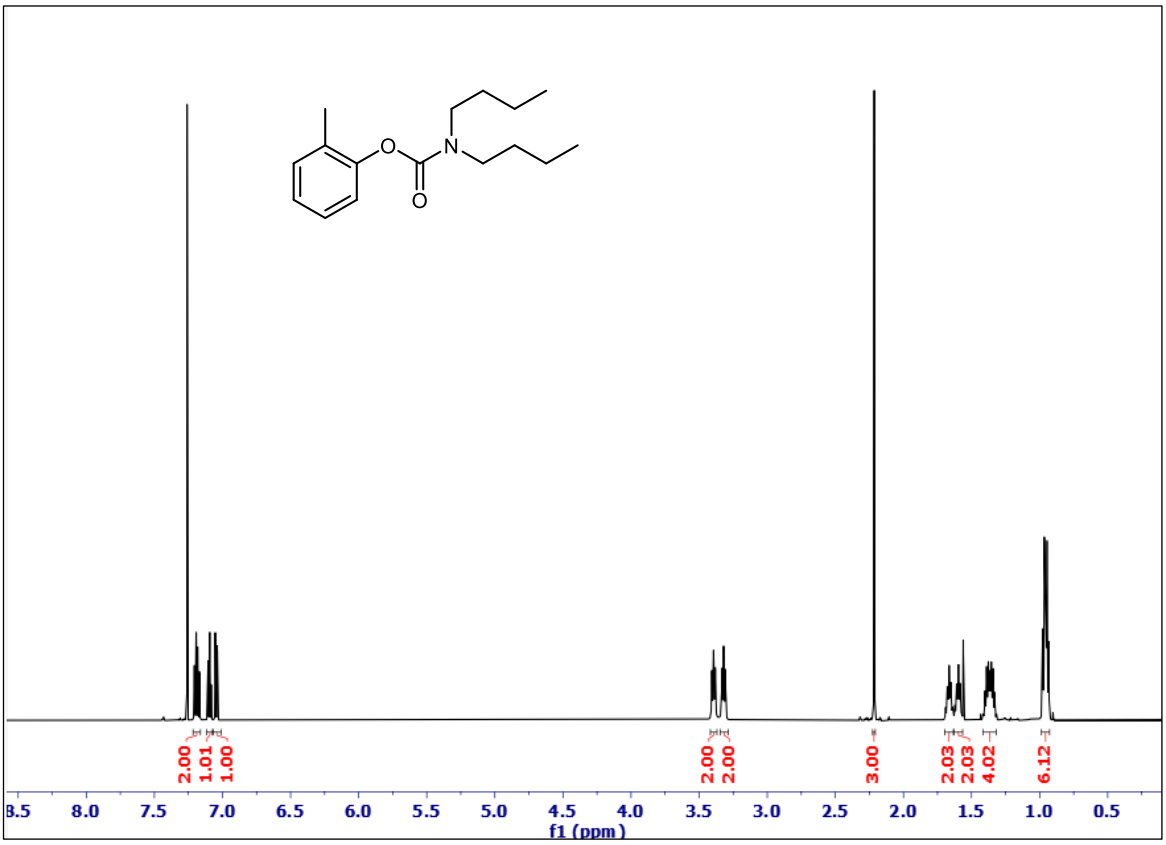


^{13}C NMR (150 MHz, $CDCl_3$)

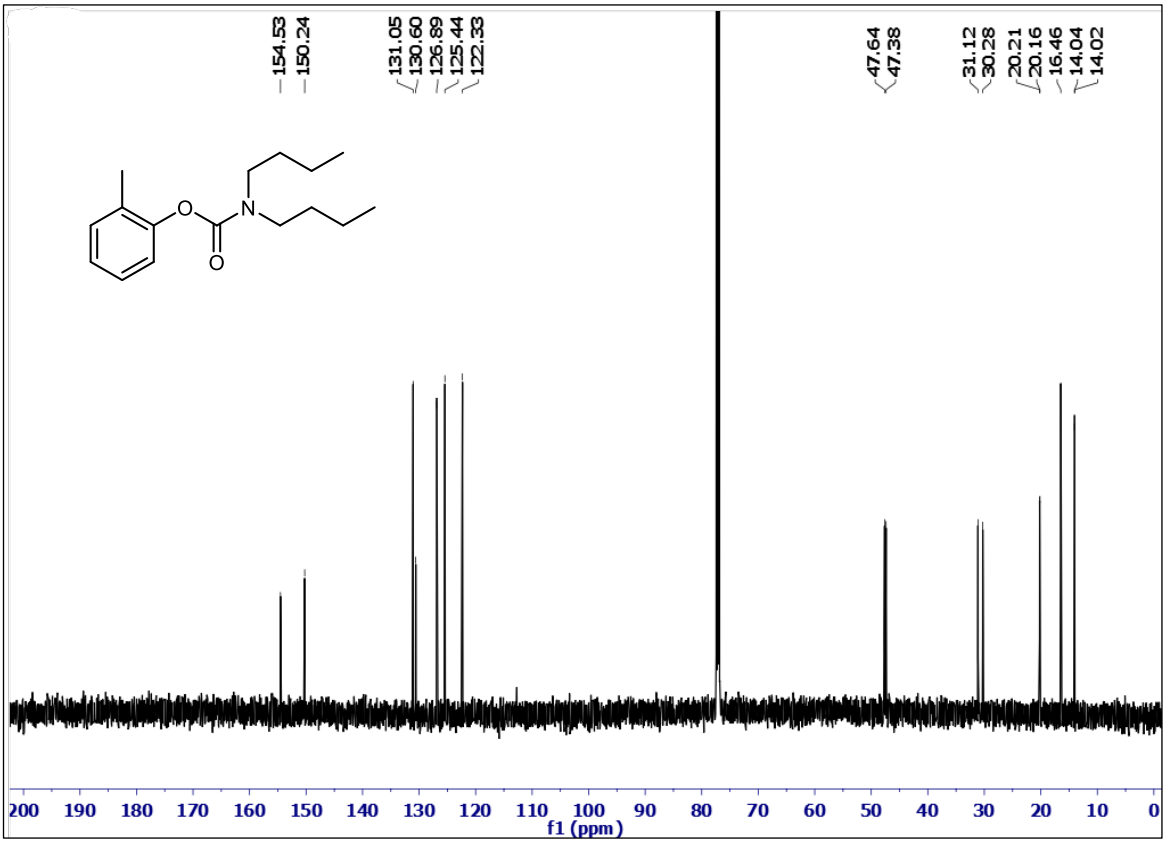


2-Methylphenyl-*N*,*N*-dibutylcarbamate (1u)

^{1}H NMR (600 MHz, $CDCl_3$)

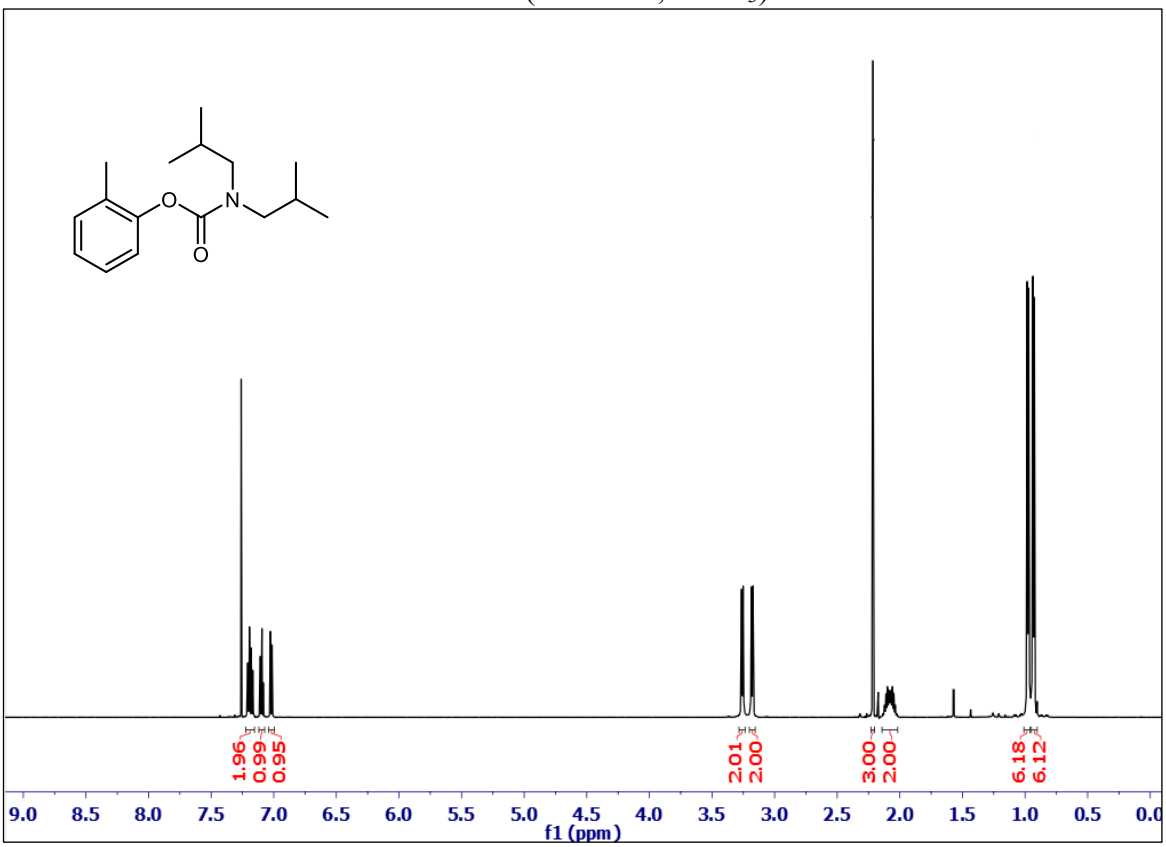


^{13}C NMR (150 MHz, $CDCl_3$)

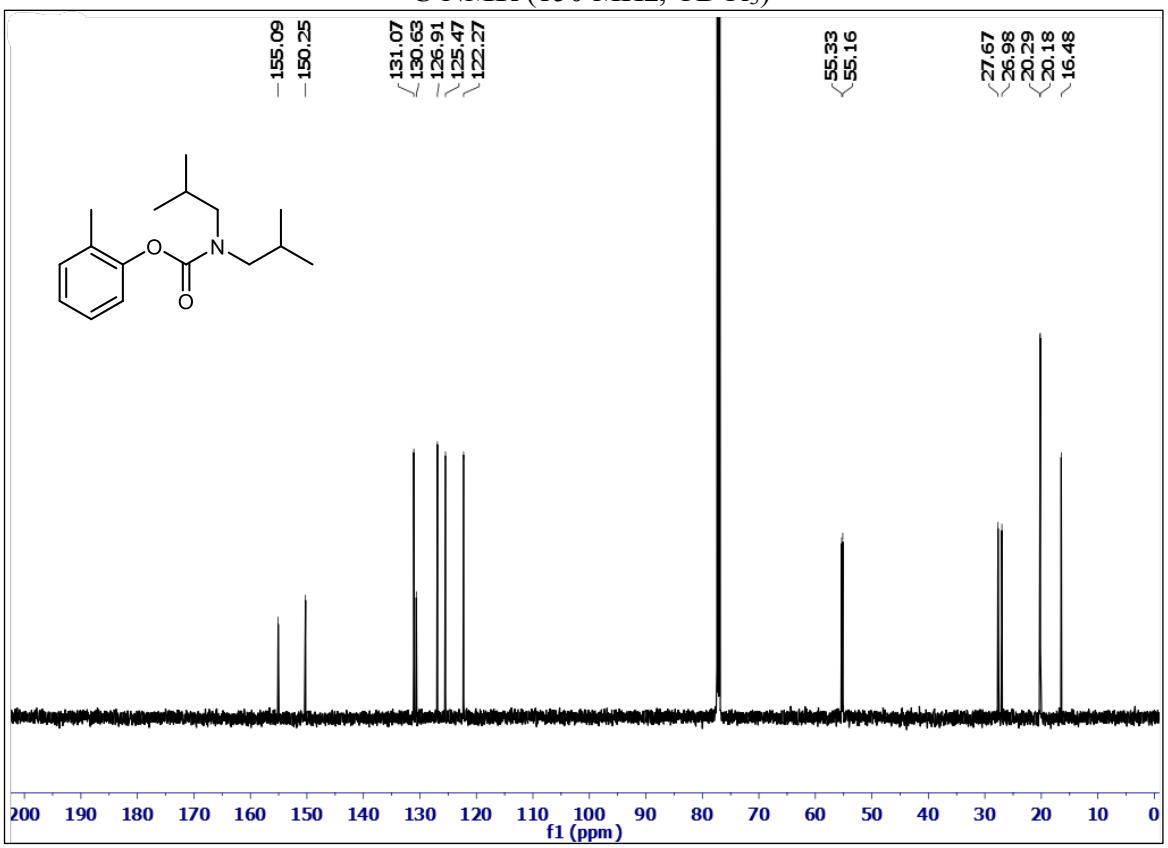


2-Methylphenyl-*N*,*N*-diisobutylcarbamate (1v)

^{1}H NMR (600 MHz, $CDCl_3$)

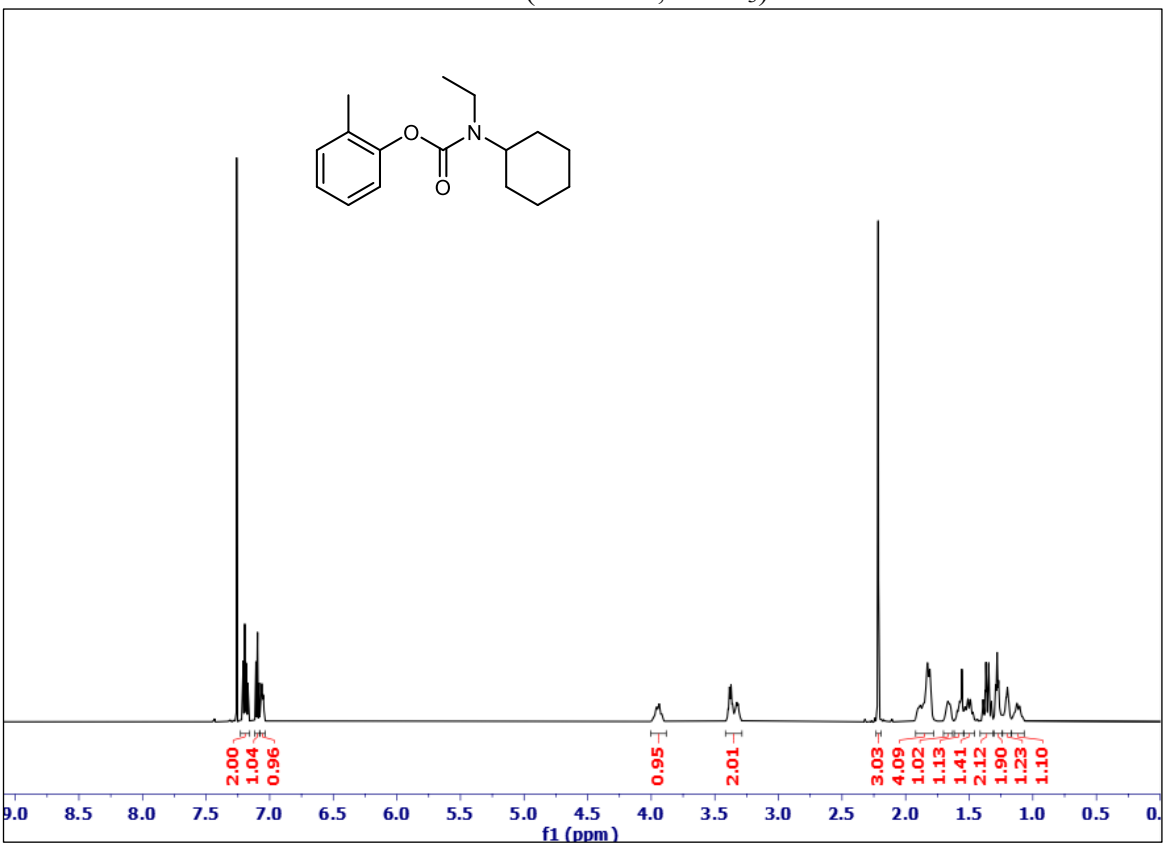


^{13}C NMR (150 MHz, $CDCl_3$)

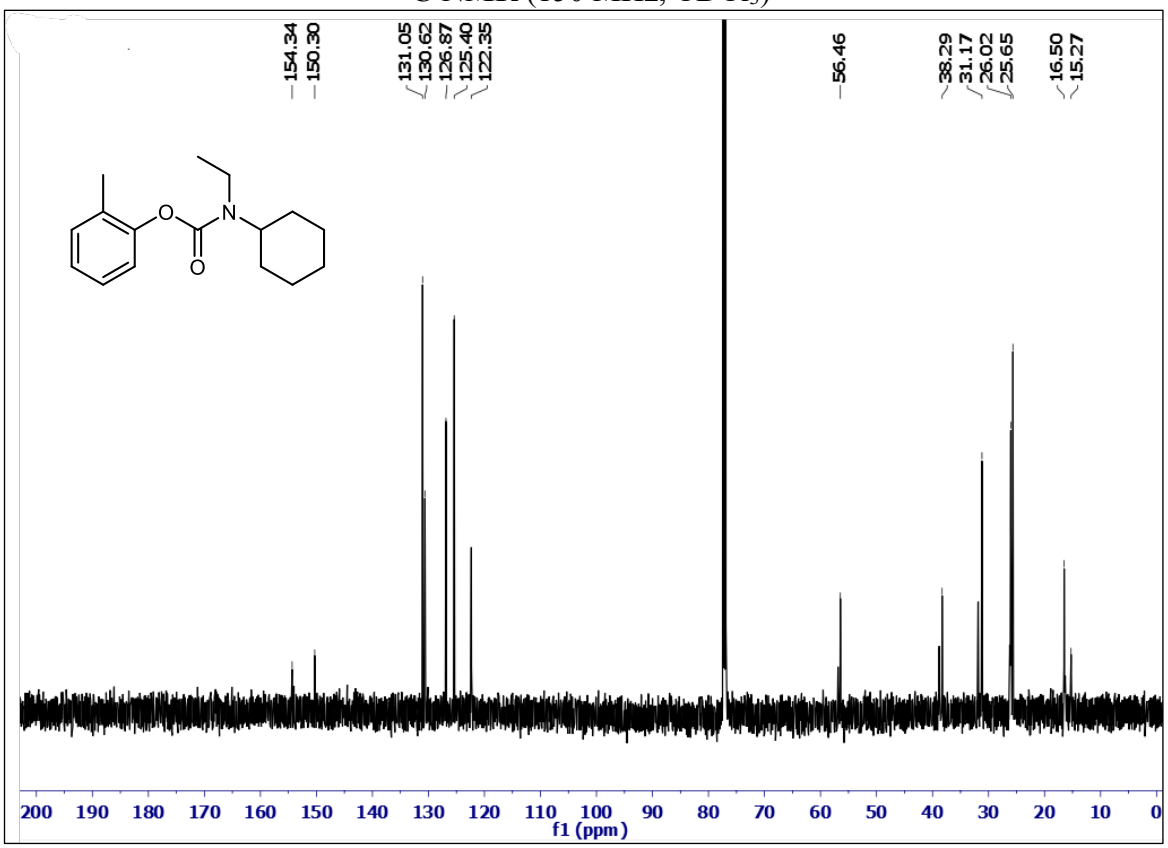


2-Methylphenyl-*N*-cyclohexyl-*N*'-ethylcarbamate (1w)

^{1}H NMR (600 MHz, $CDCl_3$)

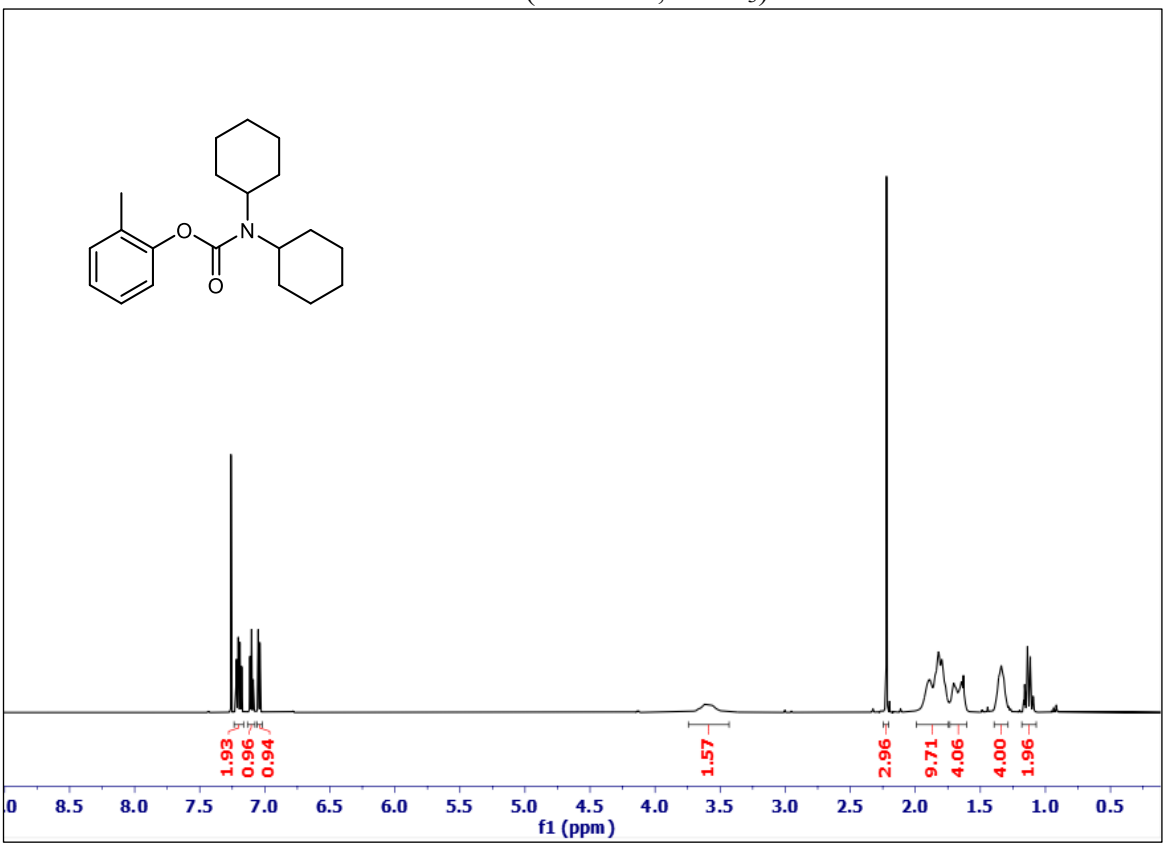


^{13}C NMR (150 MHz, $CDCl_3$)

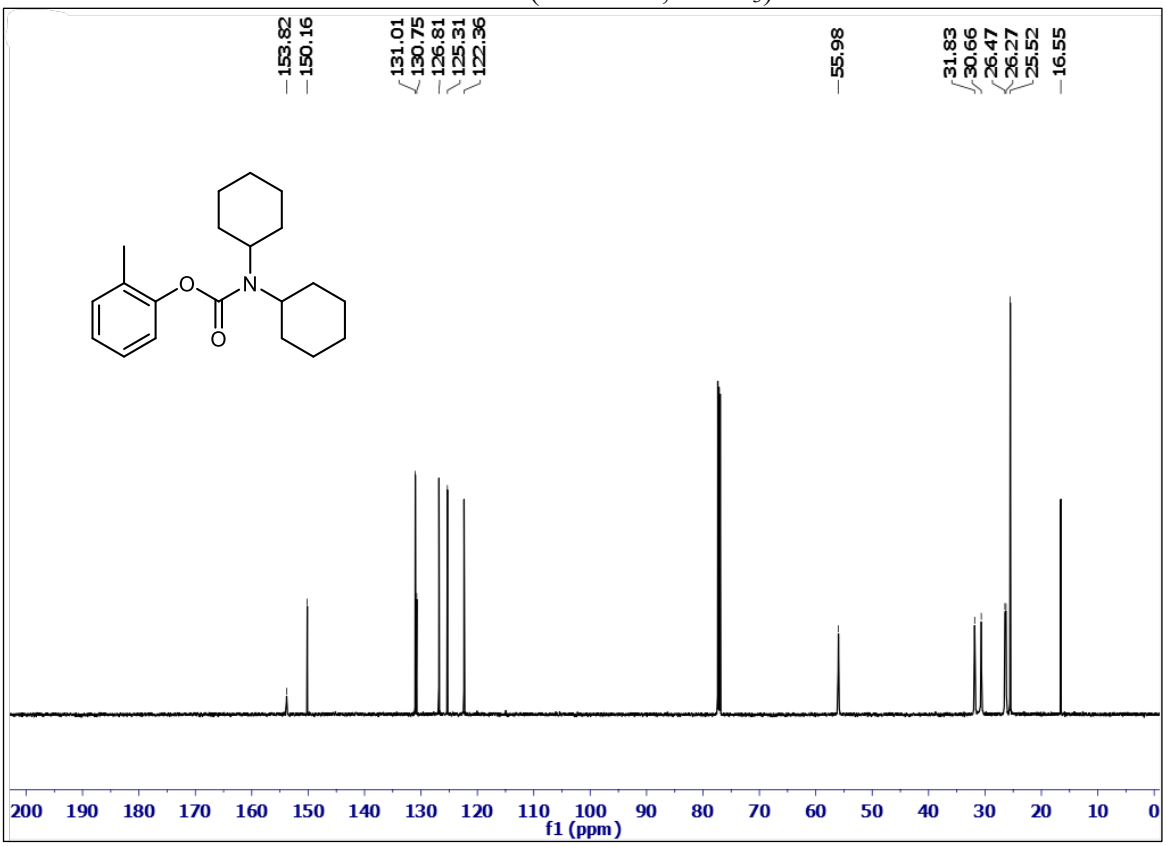


2-Methylphenyl-*N*,*N*-dicyclohexylcarbamate (1x)

^{1}H NMR (600 MHz, $CDCl_3$)

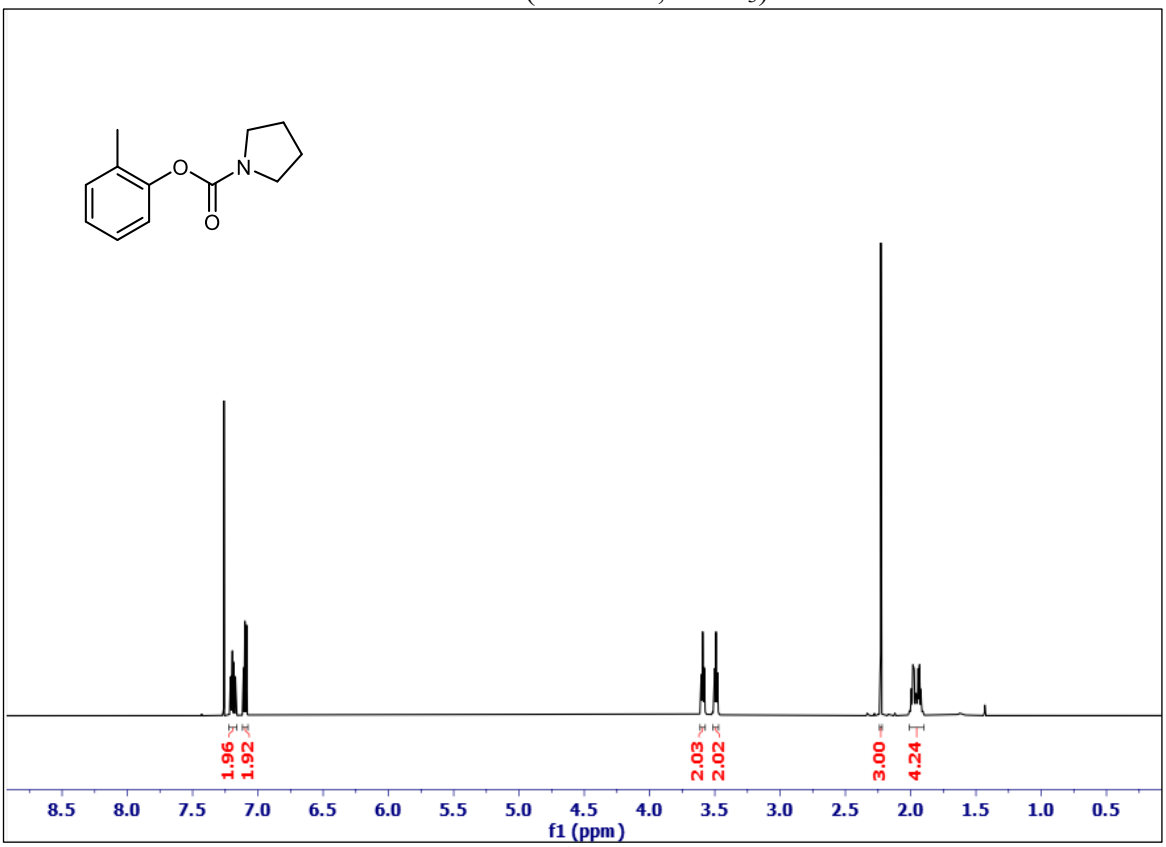


^{13}C NMR (150 MHz, $CDCl_3$)

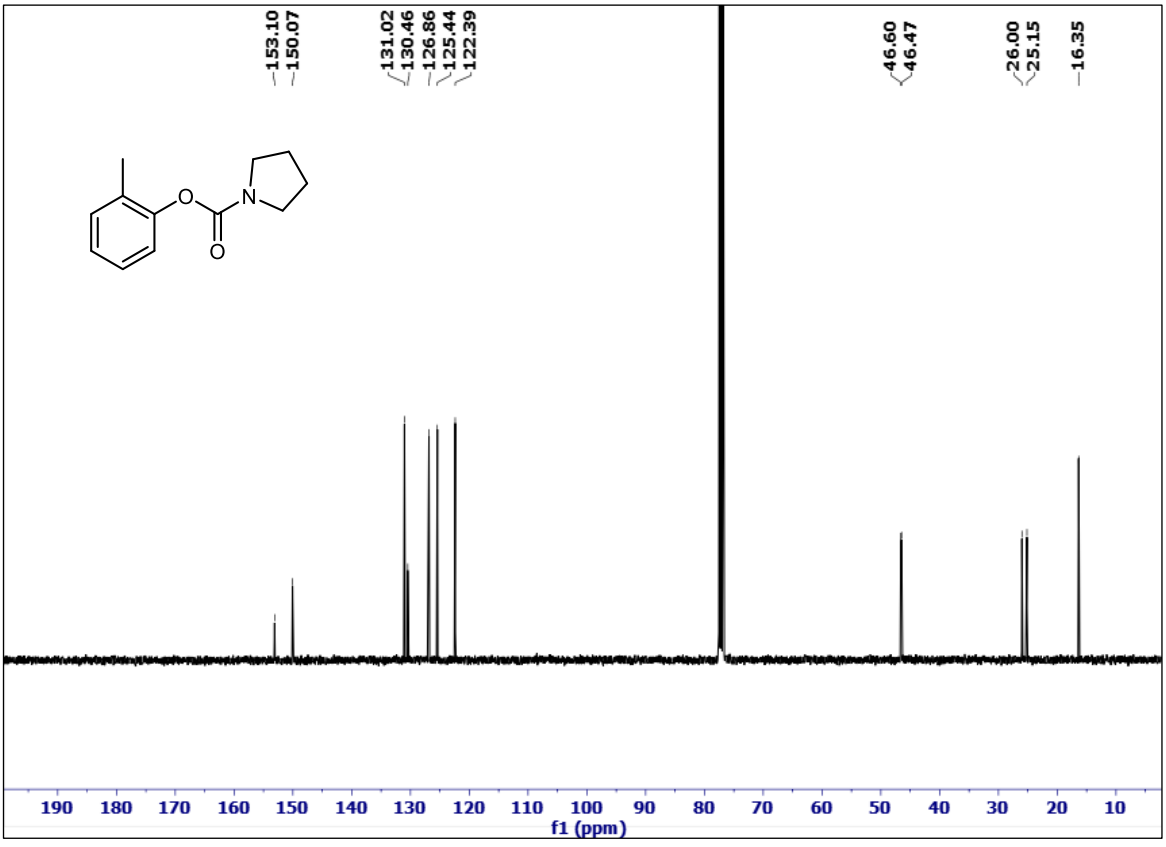


2-Methylphenyl pyrrolidine-1-carboxylate (1y)

^{1}H NMR (600 MHz, $CDCl_3$)

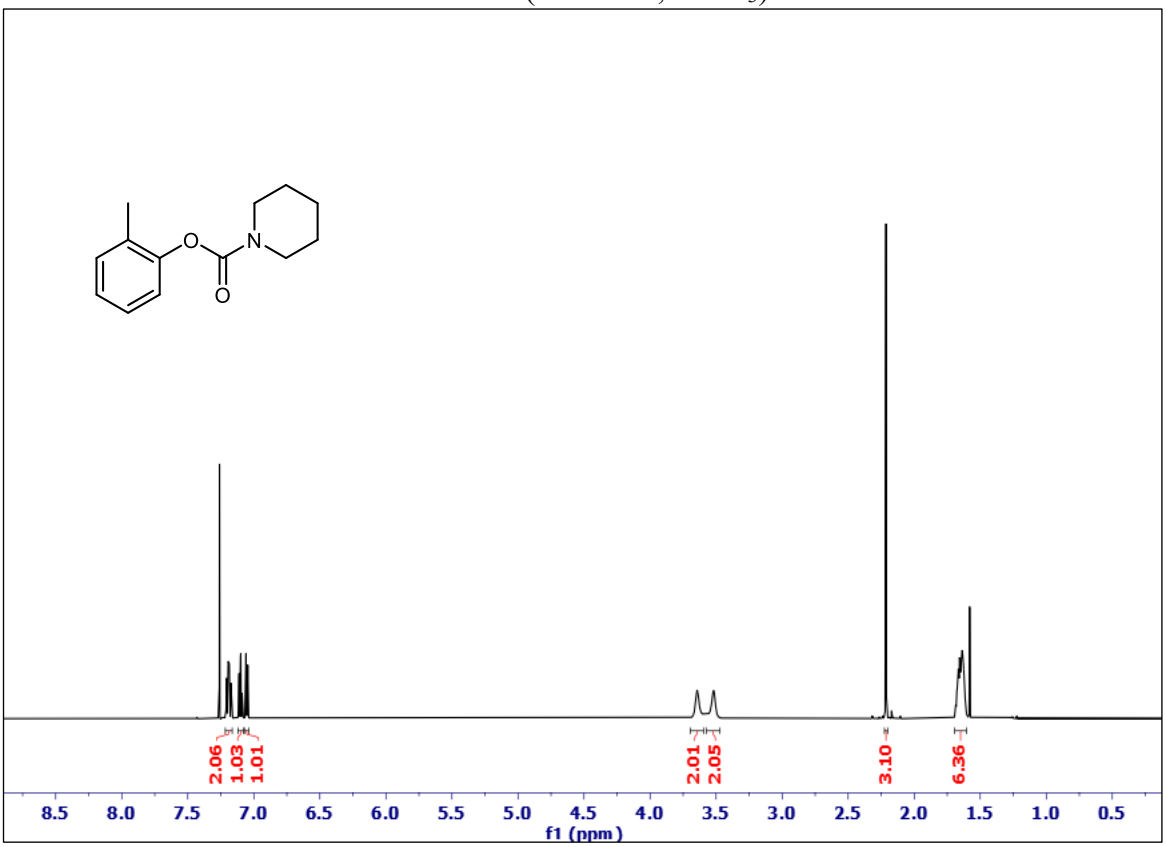


^{13}C NMR (100 MHz, $CDCl_3$)

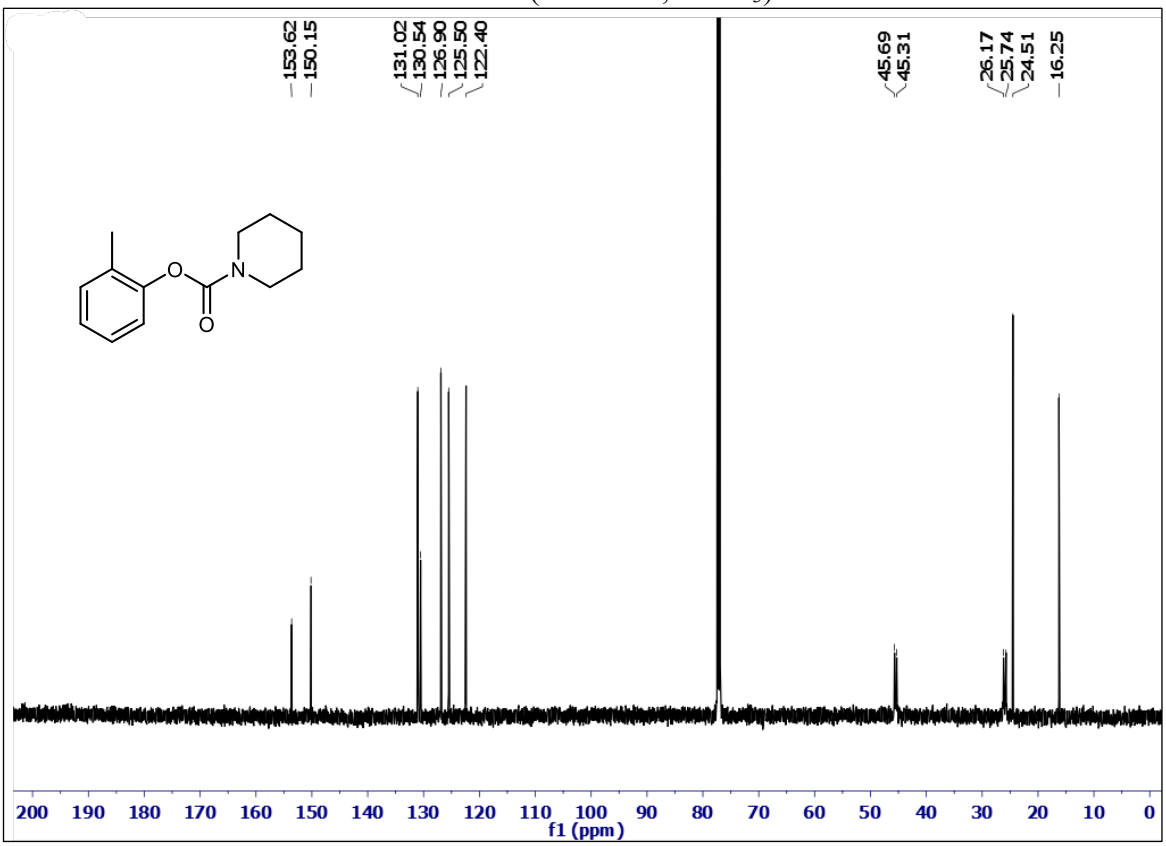


2-Methylphenyl piperidine-1-carboxylate (1z)

^{1}H NMR (600 MHz, $CDCl_3$)

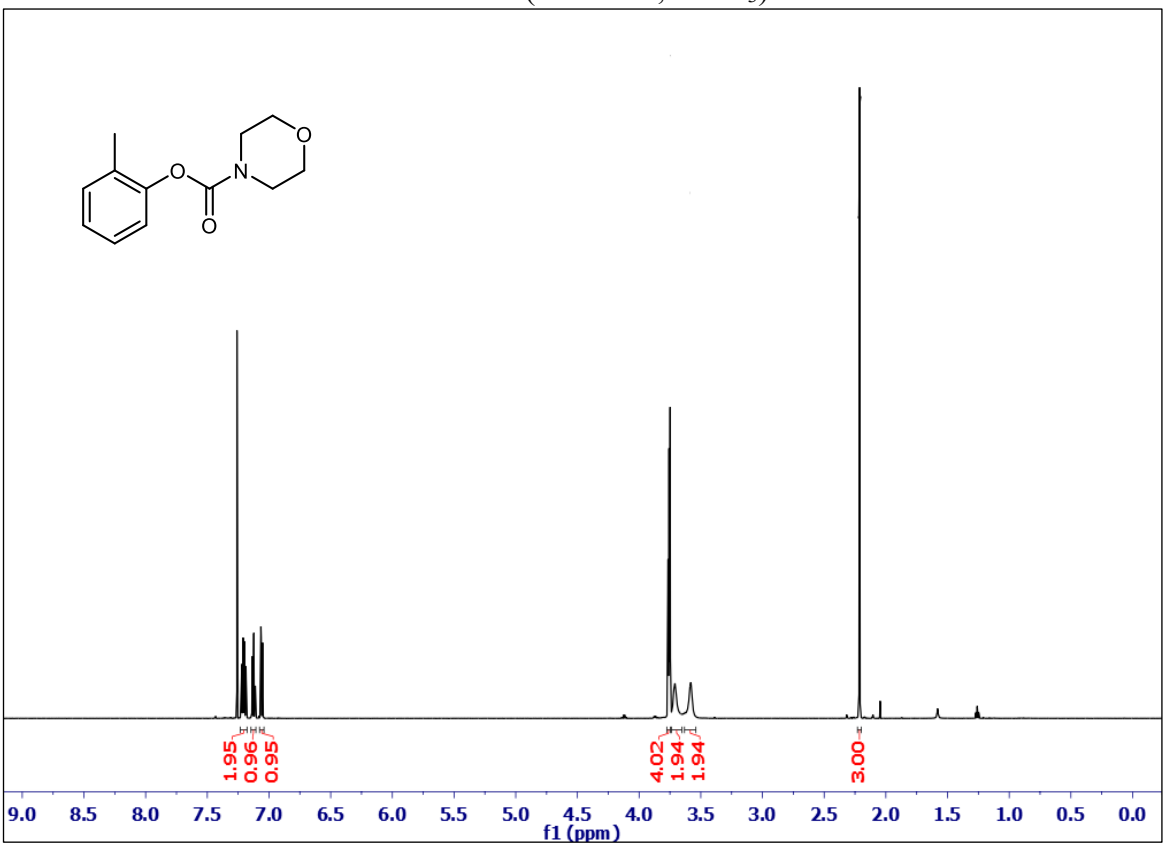


^{13}C NMR (150 MHz, $CDCl_3$)

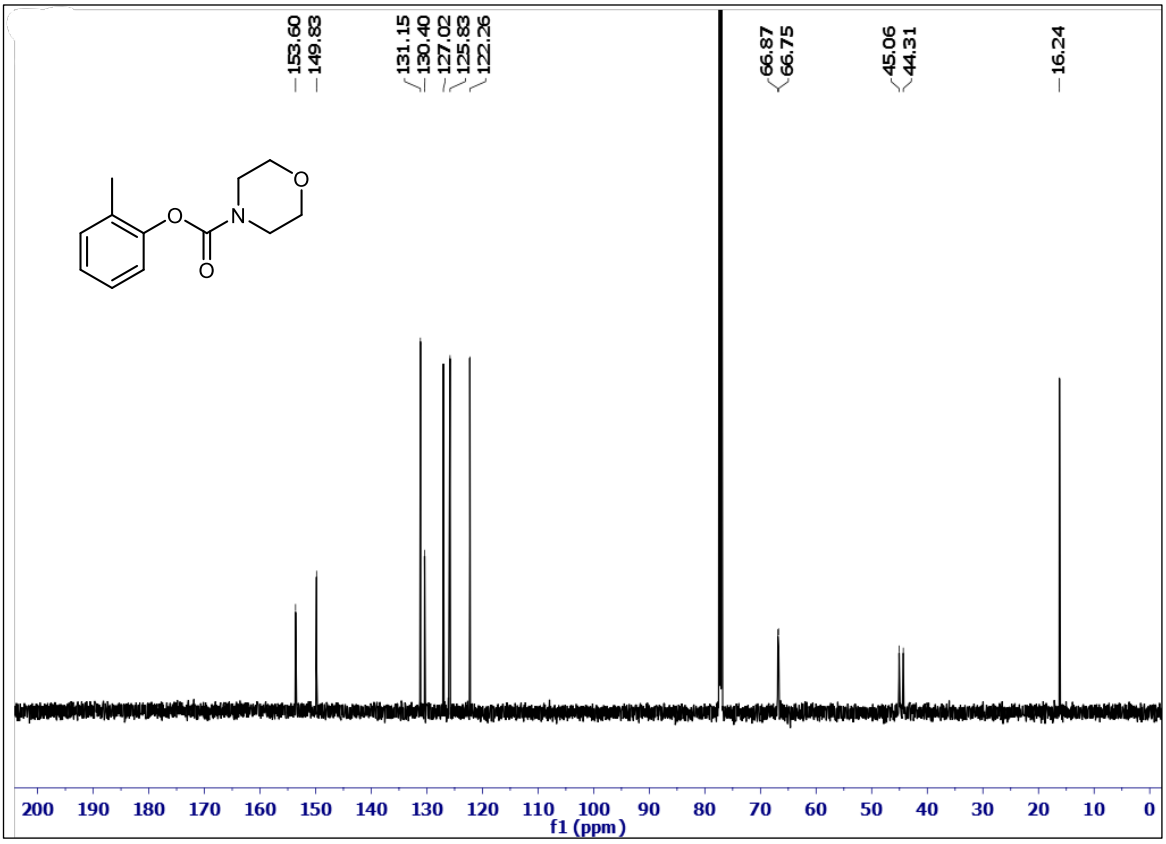


2-Methylphenyl morpholine-4-carboxylate (1aa)

^{1}H NMR (600 MHz, $CDCl_3$)

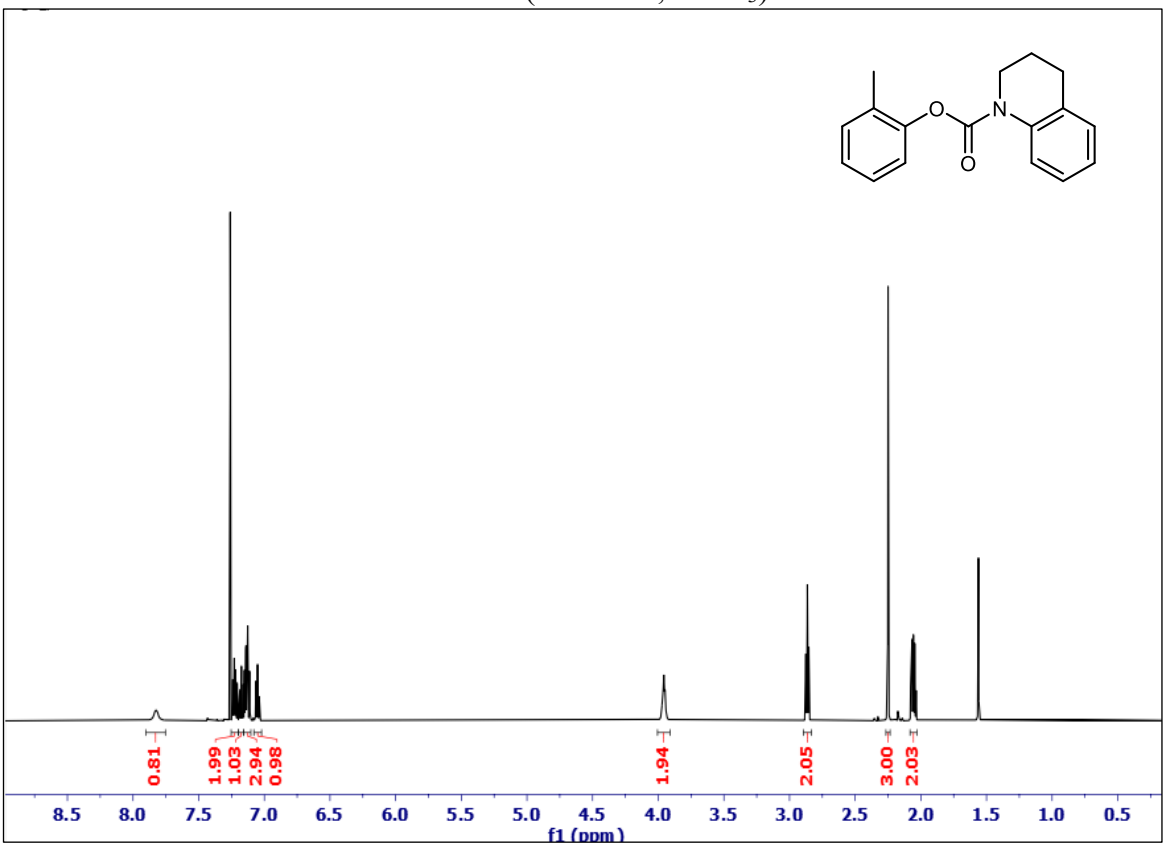


^{13}C NMR (150 MHz, $CDCl_3$)

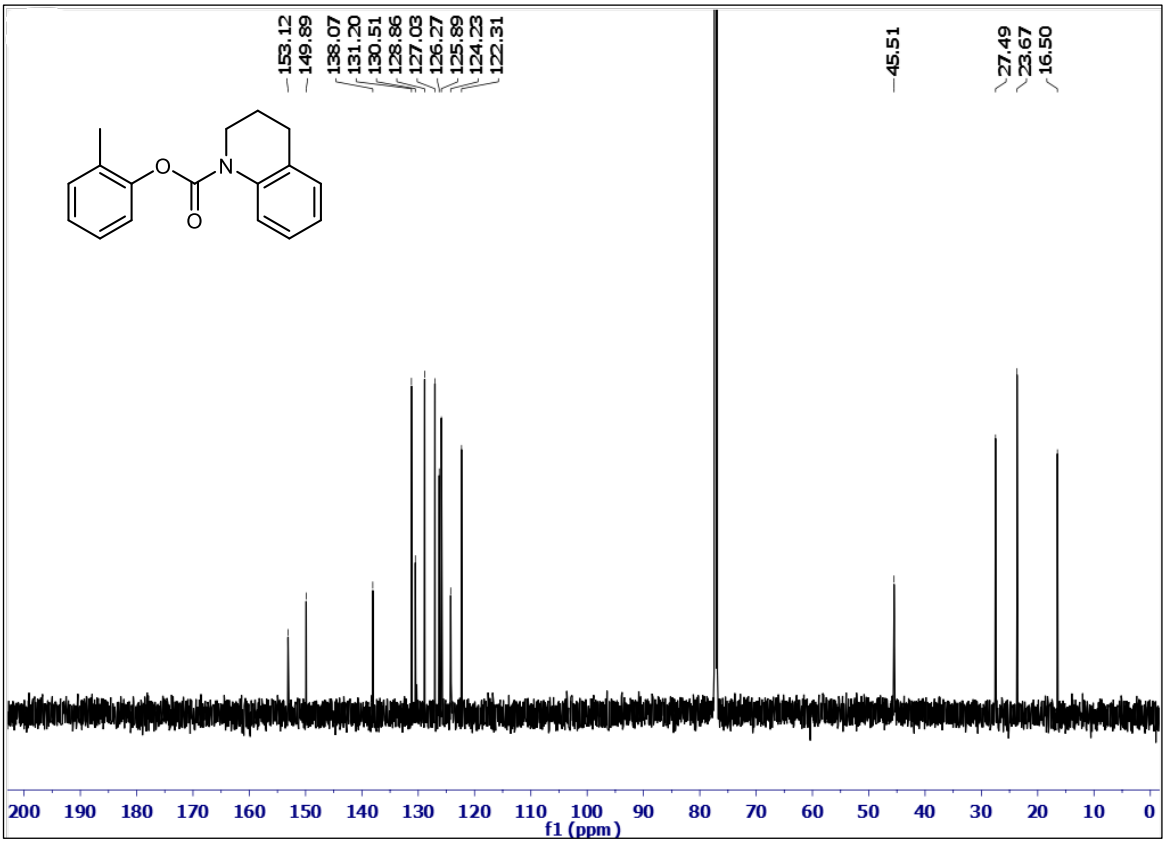


2-Methylphenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (1ab)

^{1}H NMR (600 MHz, $CDCl_3$)

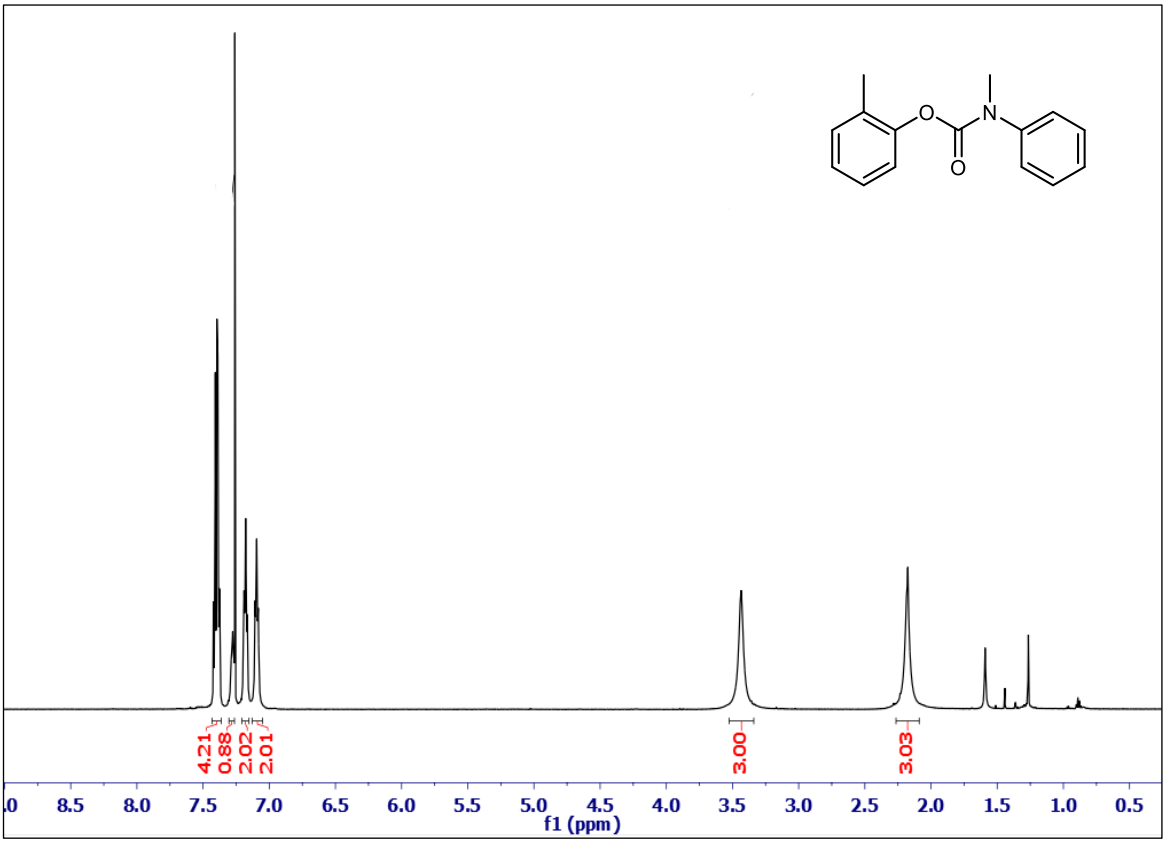


^{13}C NMR (150 MHz, $CDCl_3$)

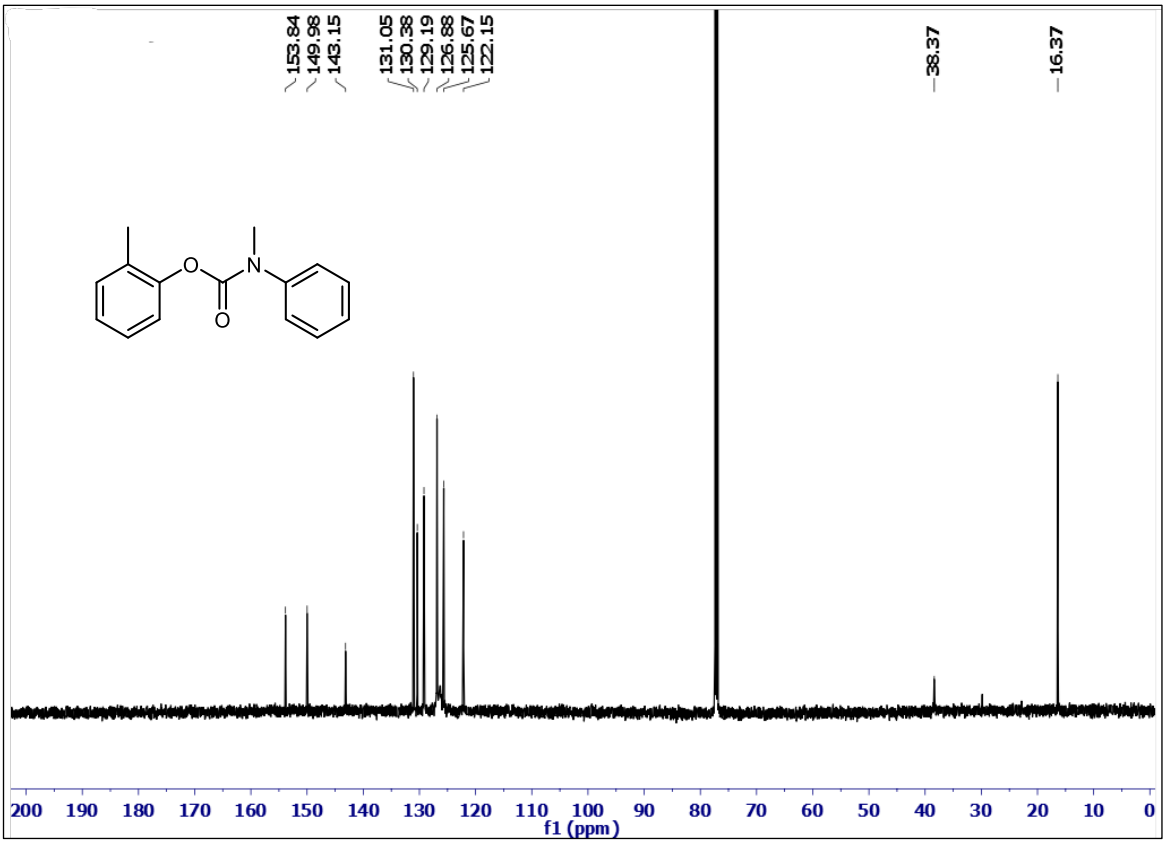


2-Methylphenyl-*N*-phenyl-*N*'-methylcarbamate (1ac)

^{1}H NMR (600 MHz, $CDCl_3$)

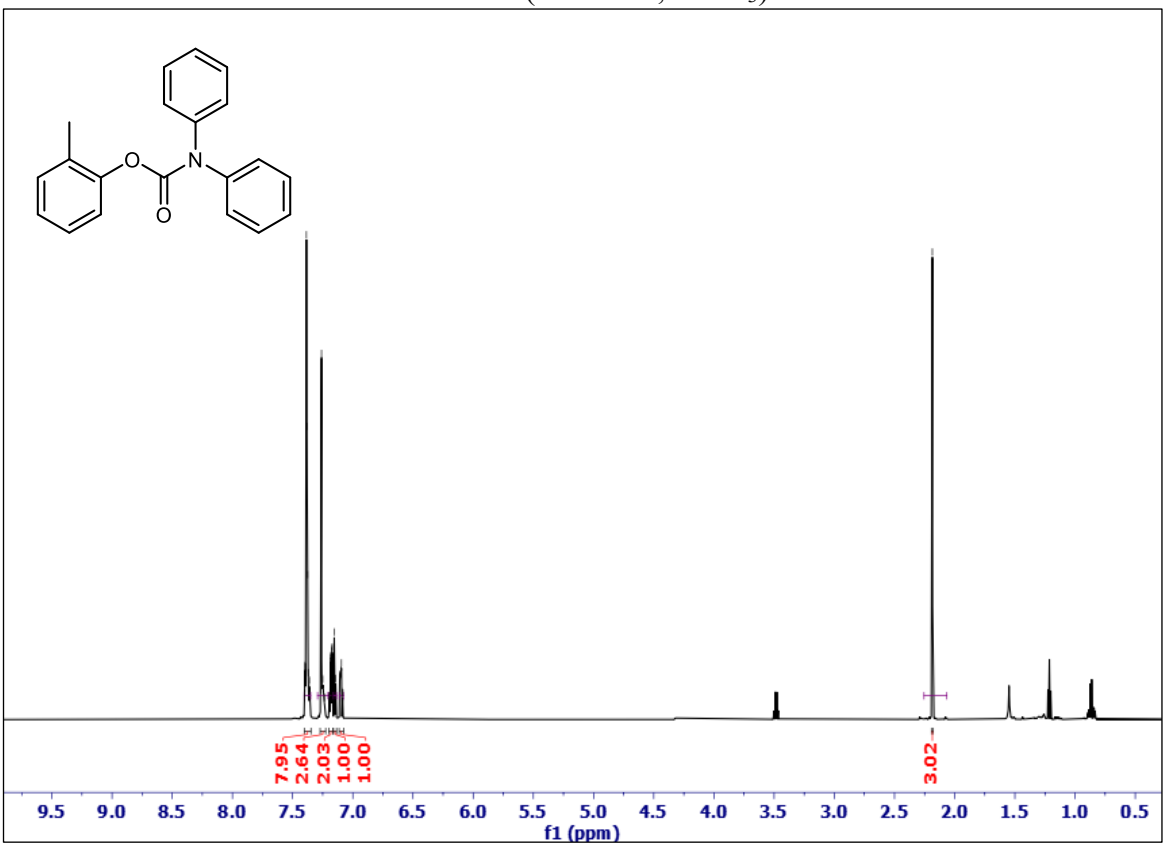


^{13}C NMR (150 MHz, $CDCl_3$)

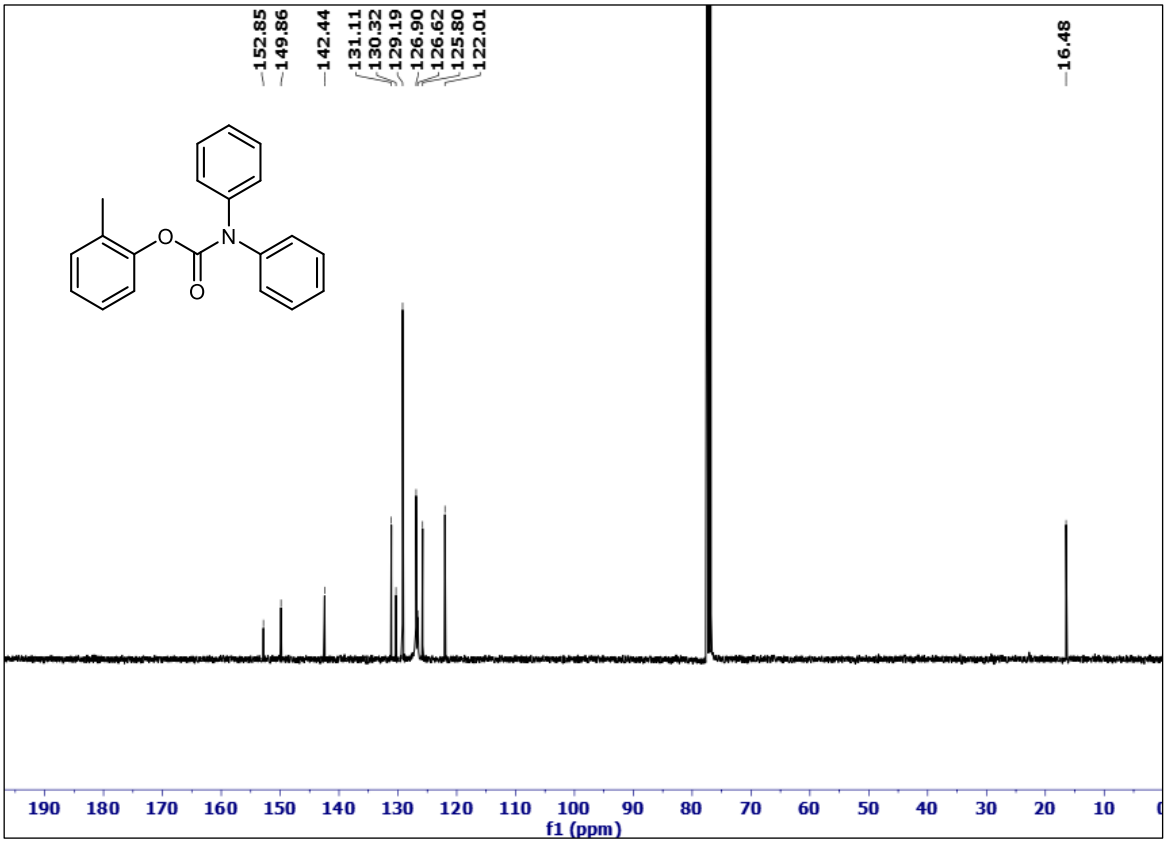


2-Methylphenyl-*N*,*N*-diphenylcarbamate (1ad)

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

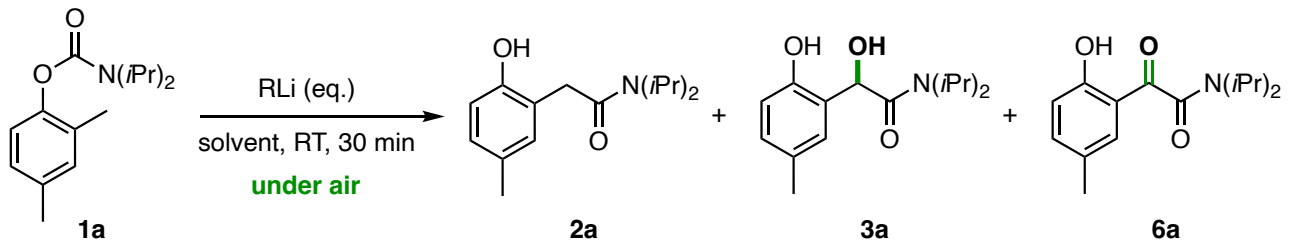


Homo-Fries rearrangement of carbamate **1a** under aerobic conditions

Reactions were performed under air at room temperature unless otherwise specified. To a stirred solution of **1a** (1.0 eq., 0.20 mmol) in the appropriate solvent (1 mL, 0.2 M), the selected base was added. The resulting reaction mixture was stirred for 30 min under air and then quenched with aqueous 2 M HCl. The mixture was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum.

Samples of **2a**, **3a** and 2-(2-hydroxy-5-methylphenyl)-*N,N*-diisopropyl-2-oxoacetamide (**6a**) were isolated by purification of entries 3, 8 and 9 (Table S1) by flash column chromatography using petroleum ether/EtOAc 9/1 or 8/2 v/v as solvent mixtures and used as reference for quantitative ^{1}H NMR analysis. Yields of **2a**, **3a** and **6a** were determined by quantitative ^{1}H NMR in CD_3OD using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor of 1 for the preparation of the sample (See Eq. 1).

Table S1. Optimization of the reaction conditions.[a]



1a **2a** **3a** **6a**

Entry[a]	RLi (eq.)	Solvent	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**6a** (%)[b]
1	LiTMP (2)	CPME	64	0	34[c]	0
2	LiTMP (2)	2-MeTHF	0	0	54	10
3	LiTMP (3)	2-MeTHF	0	0	70[c]	0
4	LiTMP (4)	2-MeTHF	0	0	64	15
5[d]	LiTMP (3)	2-MeTHF	0	0	60	14
6	LiTMP (3)	4-MeTHP	0	0	53	13
7	LiTMP (3)	DME	7	0	62	20
8	LiTMP (3)	THF	0	0	54	23
9	LiTMP (3)	Et_2O	0	35	50	0
10	LiTMP (3)	MTBE	0	17	48	0
11	LiTMP (3)	*n*-hexane	0	32	57	0
12	LiTMP (3)	1,4-dioxane	0	32	59	9
13	LDA (3)	2-MeTHF	38	0	34	6
14	*t*-BuLi (3)	2-MeTHF	0	0	32	0
15	*s*-BuLi (3)	2-MeTHF	0	10	36[e]	0

[a] Reaction conditions: **1a** (0.20 mmol), solvent (1 mL), RLi, RT, under air. CPME = cyclopentyl methyl ether, 2-MeTHF = 2-methyltetrahydrofuran, 4-MeTHP = 4-methyltetrahydropyran, DME = 1,2-dimethoxyethane, MTBE = methyl *t*-butyl ether). LiTMP (1 M in 2-MeTHF), LDA (1 M in 2-MeTHF), *t*-BuLi (1.7 M in pentane), *s*-BuLi (1.4 M in cyclohexane). [b] Determined by ^{1}H NMR using *n*-heptane as the internal standard. [c] Yield of isolated **3a** = 68%. [d] Reaction time = 45 min. [e] The *ortho*-rearranged salicylamide (45%) was observed in the crude reaction mixture.[4]

2-(2-Hydroxy-5-methylphenyl)-*N,N*-diisopropylacetamide (2a): General procedure starting from **1a** (1.0 eq., 0.20 mmol, 50 mg). Conditions reported in Table S1, entry 9. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 9/1 v/v) gave **2a** as a white solid (16.5 mg, 33%, R_f = 0.28 petroleum ether/Et_2O 9/1 v/v), mp. 163.5-166.1 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 6.93 (d, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 8.1, 1.3 Hz 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 4.11 (sept, *J* = 6.7 Hz, 1H), 3.61 (s, 2H), 3.47 (br s, 1H), 2.21 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.03 (d, *J* = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 173.8, 153.6, 130.8, 129.8, 129.4, 122.8, 116.3, 51.0, 47.1, 37.7, 20.8, 20.6, 20.6. EI-MS m/z (%): 249 (M+, 53), 148 (16), 121 (30), 86 (100), 43 (33). HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_2$+H^+: 250.1802 [M+H^+]; found: 250.1802. All analytical data were in good accordance with those reported in the literature.[4]

2-Hydroxy-2-(2-hydroxy-5-methylphenyl)-*N,N*-diisopropylacetamide (3a): General procedure starting from **1a** (1.0 eq., 0.20 mmol, 50 mg). Conditions reported in Table S1, entry 3. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 8/2 v/v) gave **3a** as a white solid (36 mg, 68%, R_f = 0.25 petroleum ether/EtOAc 8/2 v/v), mp. 179.0-181.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 8.2, 2.2, Hz, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.55 (br s, 1H), 5.34 (s, 1H), 4.68 (d, 1H), 3.88 (sept, *J* = 6.6 Hz, 1H), 3.45 (quint, *J*= 6.8 Hz, 1H), 2.24 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.7 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.4, 152.8, 130.4, 129.7, 128.8, 124.5, 117.4, 69.0, 48.3, 46.7, 20.7, 20.5, 20.4, 19.8, 19.1.

^{1}H NMR (600 MHz, CD_3OD) δ 6.96 (ddd, *J* = 8.2, 2.3, 0.7 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 5.59 (s, 1H), 3.95 (sept, *J* = 6.6 Hz, 1H), 3.44 (sept, *J* = 6.8 Hz, 1H), 2.20 (s, 3H), 1.45 (d, *J* = 6.8 Hz, 3H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H), 0.53 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 173.3, 153.4, 131.0, 130.2, 129.3, 127.1, 116.5, 66.4, 47.3, 21.0, 20.7, 20.5, 19.9, 19.0.

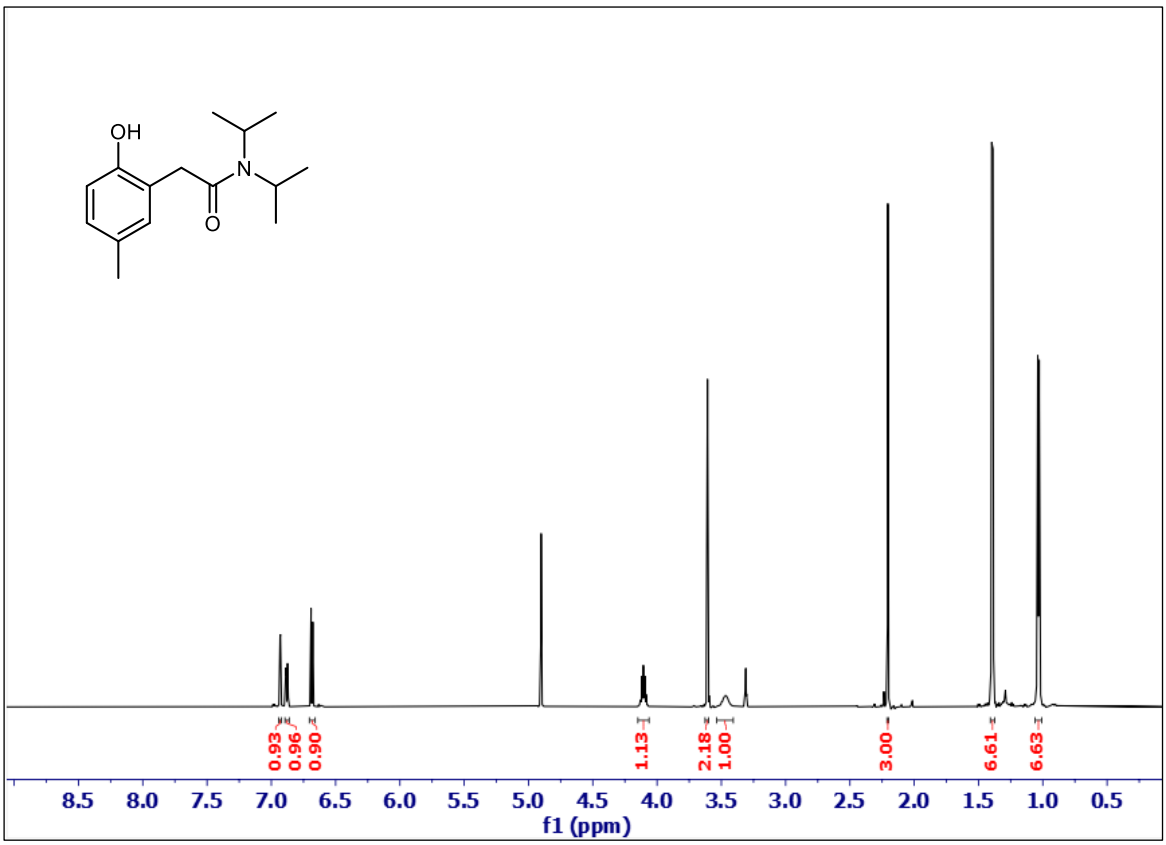
HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_3$ + Na^+: 288.1576 [M+Na^+]; found 288.1577.

2-(2-Hydroxy-5-methylphenyl)-*N,N*-diisopropyl-2-oxoacetamide (6a): General procedure starting from **1a** (1.0 eq., 0.20 mmol, 50 mg) and LiTMP (3.0 eq., 1 M in 2-MeTHF) in THF (1 mL). Condition reported in Table S1, entry 8. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 9/1 v/v) gave **6a** as a white solid (10.5 mg, 20%, R_f = 0.45 petroleum ether/EtOAc 9/1 v/v), mp. 137.0-140.0 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.41 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.38 (d, *J* = 2.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.71 (non, *J* = 13.7, 6.7 Hz, 2H), 2.29 (s, 3H), 1.54 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 195.5, 168.1, 161.5, 139.7, 131.9, 130.4, 119.0, 118.6, 52.4, 47.3, 20.4. HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NO_3$ + H^+: 264.1594 [M+H^+]; found 264.1601.

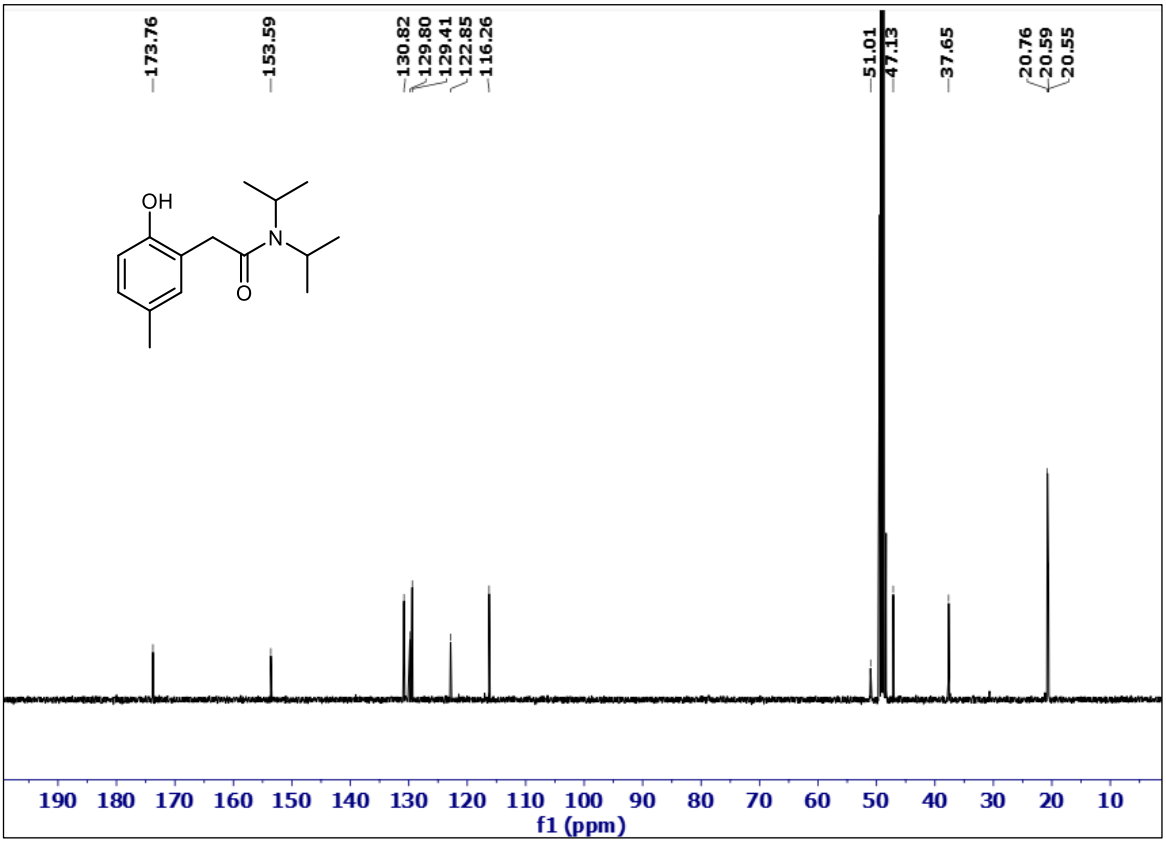
Scale up of the reaction according to the conditions reported in Table S1, entry 3. Reaction conditions: **1a** (4.0 mmol, 1.0 g), LiTMP (1 M in 2-MeTHF, 12.0 mmol, 12 mL) in 2-MeTHF (20 mL), RT, 30 min, under air. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 8/2 v/v, R_f = 0.25) gave **3a** as a white solid (700 mg, 66%).

2-(2-Hydroxy-5-methylphenyl)-*N*,*N*-diisopropylacetamide (2a)

^{1}H NMR (600 MHz, CD_3OD)

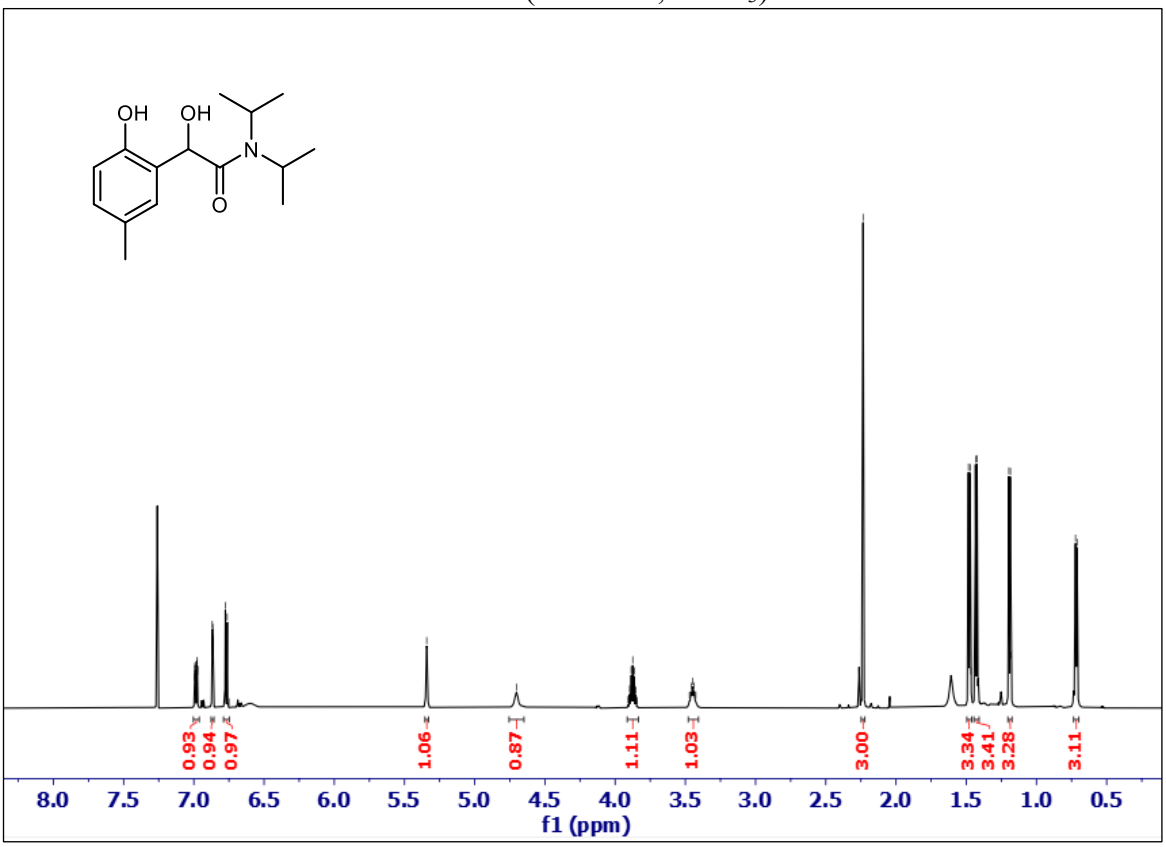


^{13}C NMR (100 MHz, CD_3OD)

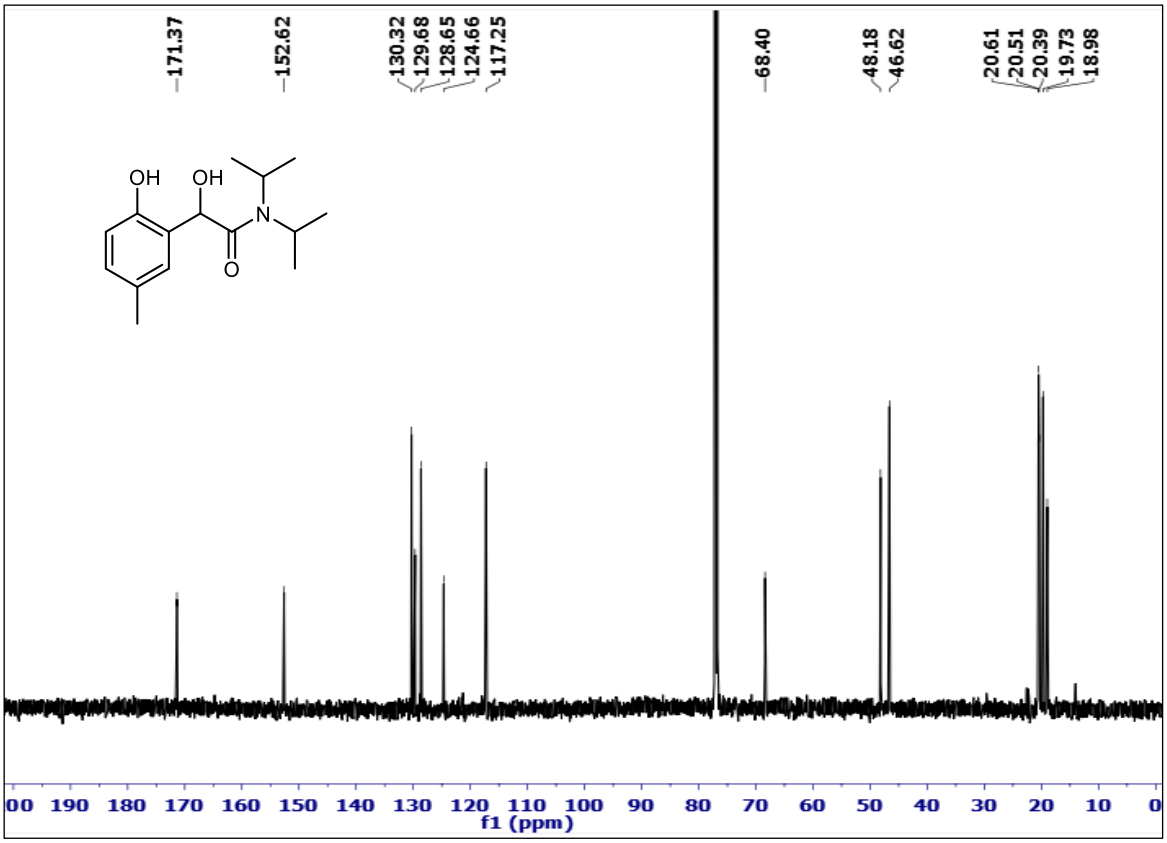


2-Hydroxy-2-(2-hydroxy-5-methylphenyl)-*N*,*N*-diisopropylacetamide (3a)

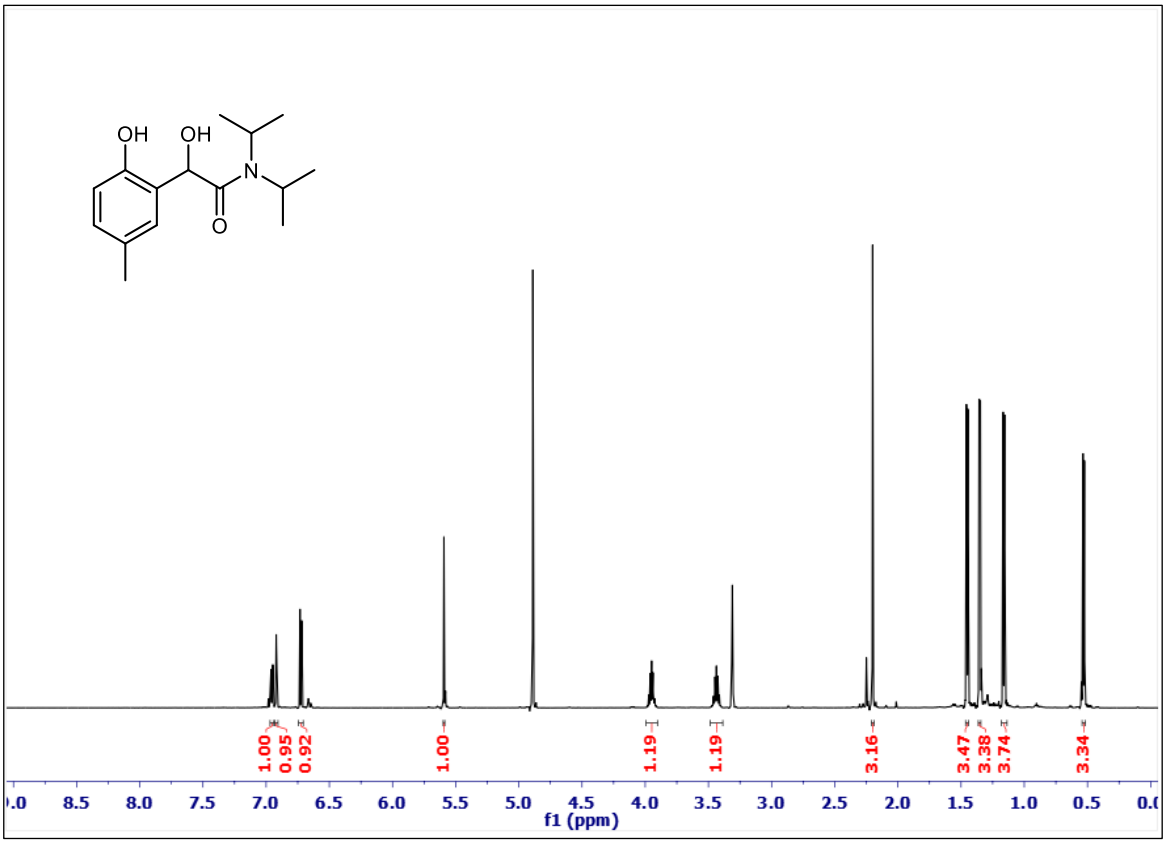
^{1}H NMR (600 MHz, $CDCl_3$)



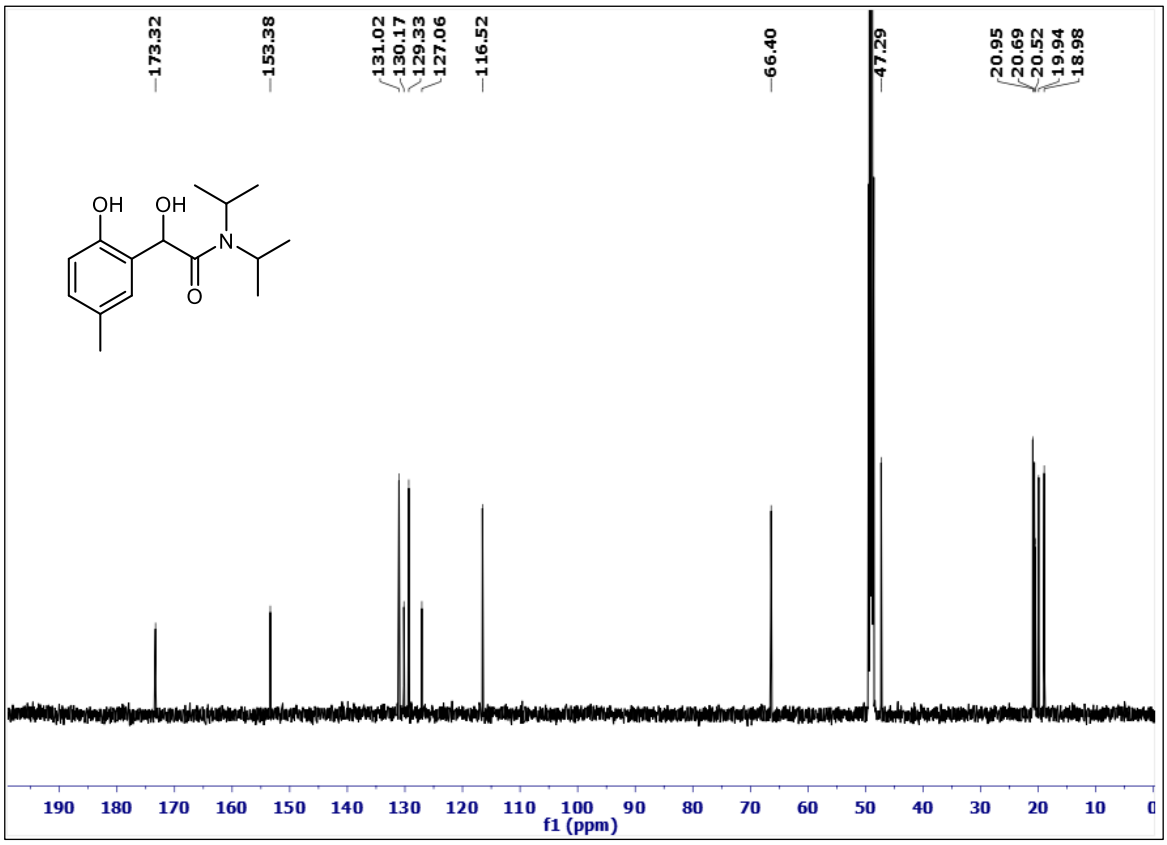
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, CD_3OD)

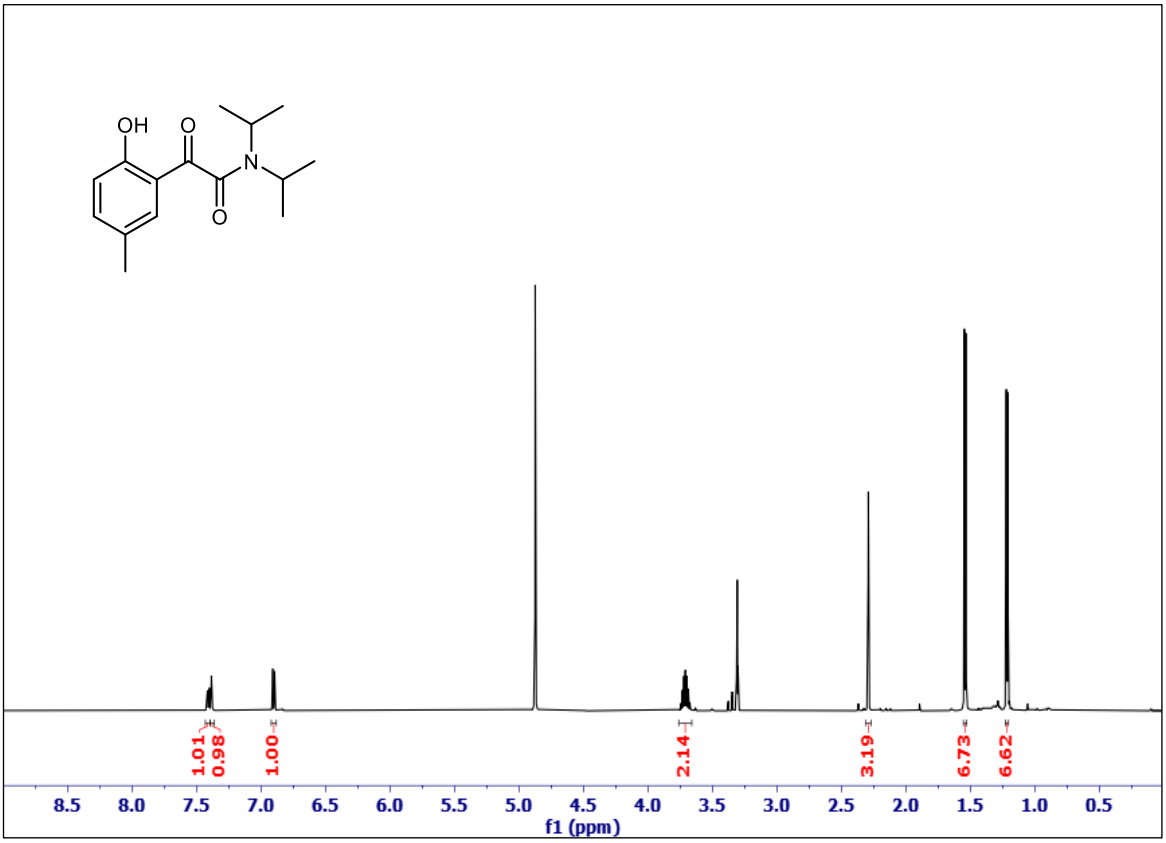


^{13}C NMR (150 MHz, CD_3OD)

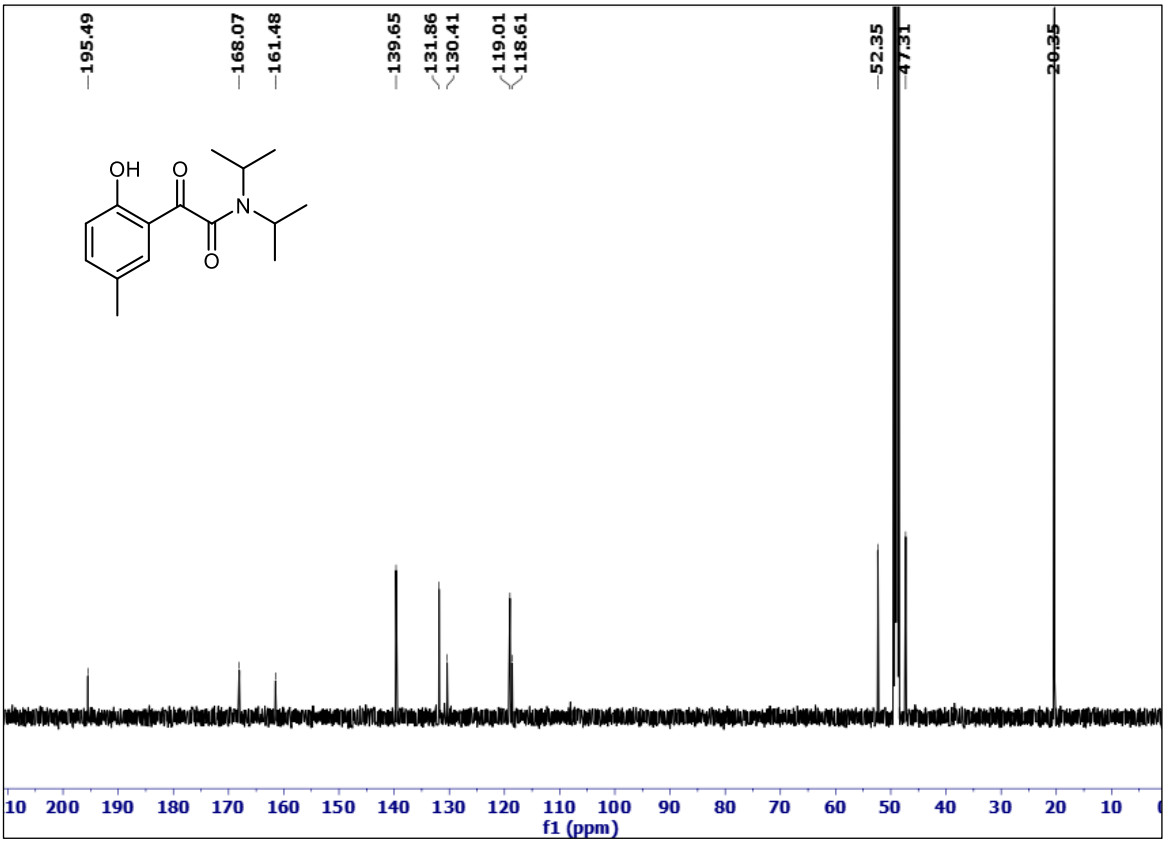


2-(2-Hydroxy-5-methylphenyl)-*N*,*N*-diisopropyl-2-oxoacetamide (6a)

^{1}H NMR (600 MHz, CD_3OD)



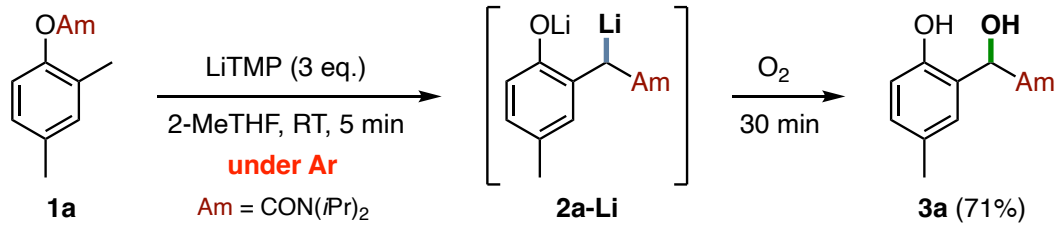
^{13}C NMR (150 MHz, CD_3OD)



*Reproducibility of the reaction: impact of the moisture content on the yield of **3a***

Rearrangement/oxidation of **1a** in the absence of moisture

Experiment 1



A solution of **1a** (1.0 eq., 0.2 mmol) in dry 2-MeTHF (1 mL) was treated with LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) at room temperature under dried Ar atmosphere. After 5 min the flask was saturated with O_2, the resulting reaction mixture was stirred for 30 min and then quenched with aqueous 2 M HCl. The mixture was extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The yield of **3a** (71%) was determined by quantitative ^{1}H NMR in CD_3OD using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor of 1 for the preparation of the sample (See Eq. 1).

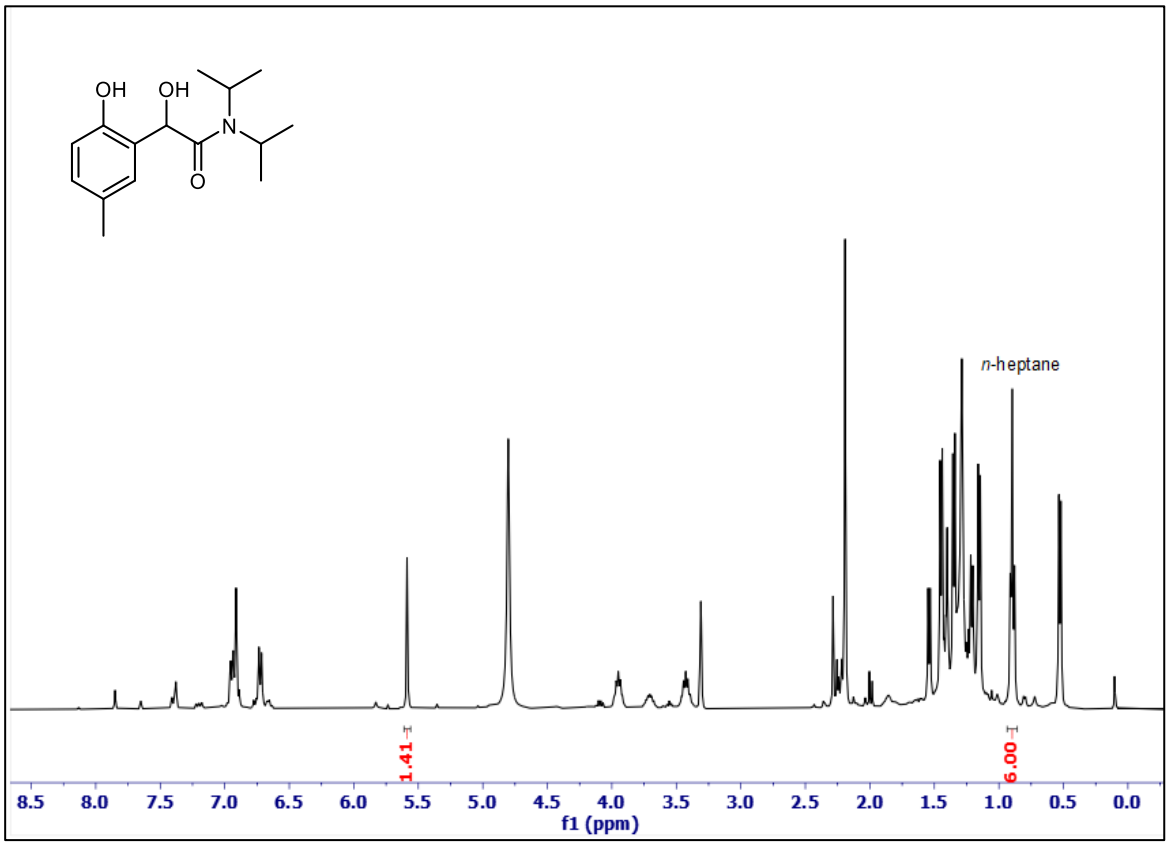
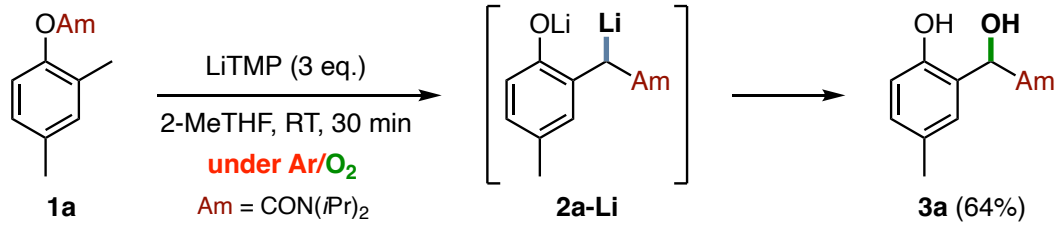


Figure S1: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **1a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mL) at RT under Ar, followed by O_2. Yield **3a**: 71%.

Experiment 2



A solution of **1a** (1.0 eq., 0.2 mmol) in dry 2-MeTHF (1 mL) under Ar was saturated with O_2 and then treated with LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) at room temperature. The resulting reaction mixture was stirred for 30 min and then quenched with aqueous 2 M HCl. The mixture was extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The yield of **3a** (64%) was determined by quantitative ^{1}H NMR in CD_3OD using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor of 1 for the preparation of the sample (See Eq. 1).

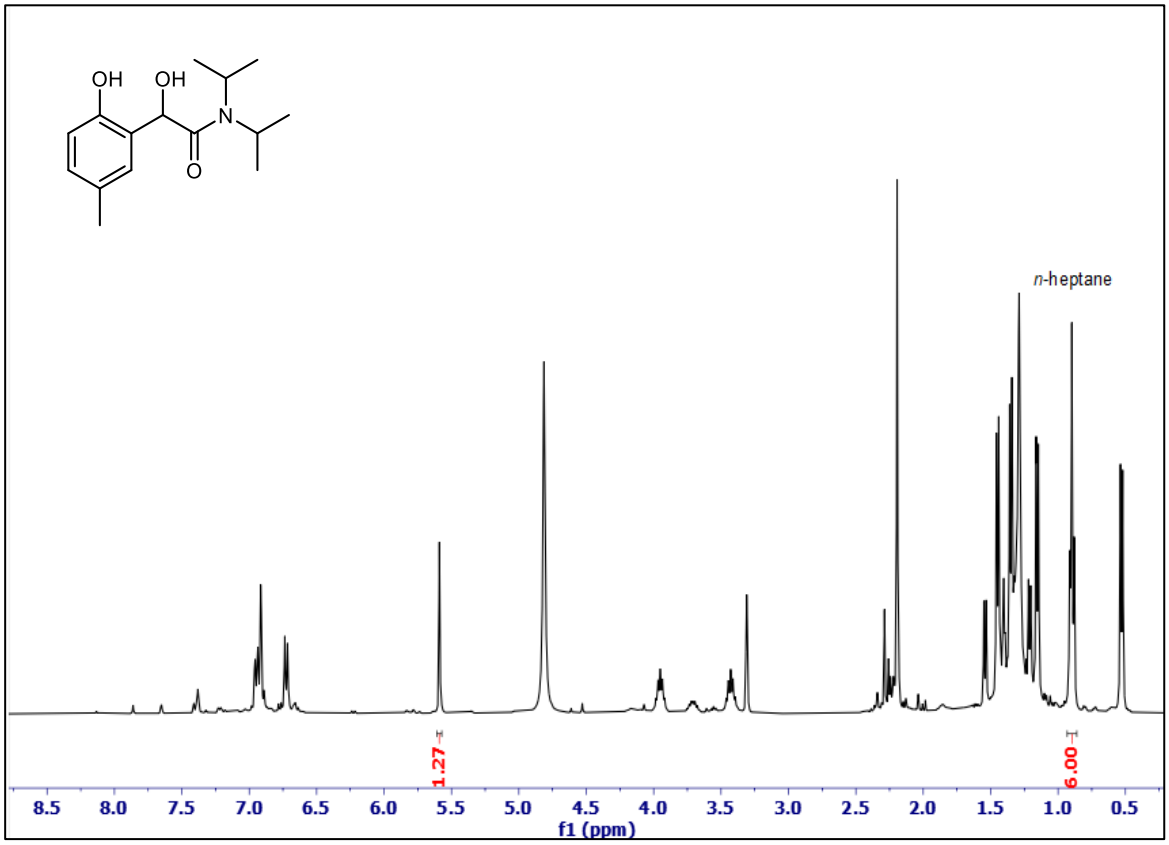
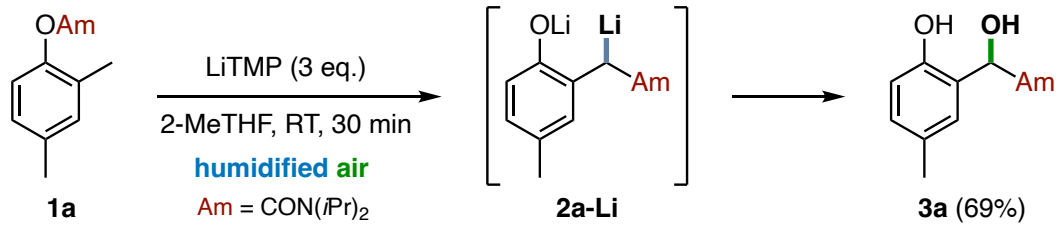


Figure S2: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **1a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mL) at RT under Ar/O_2. Yield **3a**: 64%.

Rearrangement/oxidation of **1a** in the presence of humidified air



A two-necked flask was continuously flushed with humidified air until a relative humidity level of 82% is reached (1 h). Then a solution of **1a** (1.0 eq., 0.2 mmol) in 2-MeTHF (1 mL) was added, followed by LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL), the resulting reaction mixture was stirred for 30 min at room temperature and then quenched with aqueous 2 M HCl. The mixture was extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The yield of **3a** (69%) was determined by quantitative ^{1}H NMR in CD_3OD using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor of 1 for the preparation of the sample (See Eq. 1).

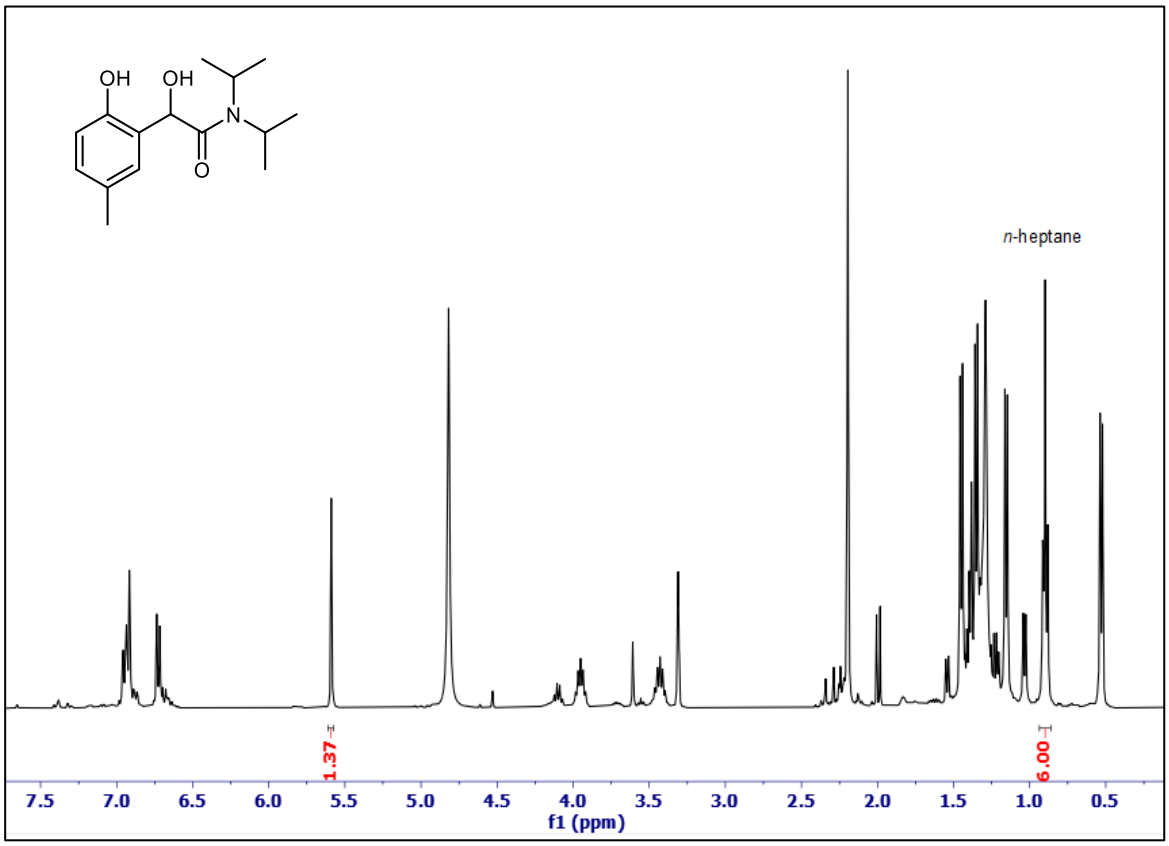
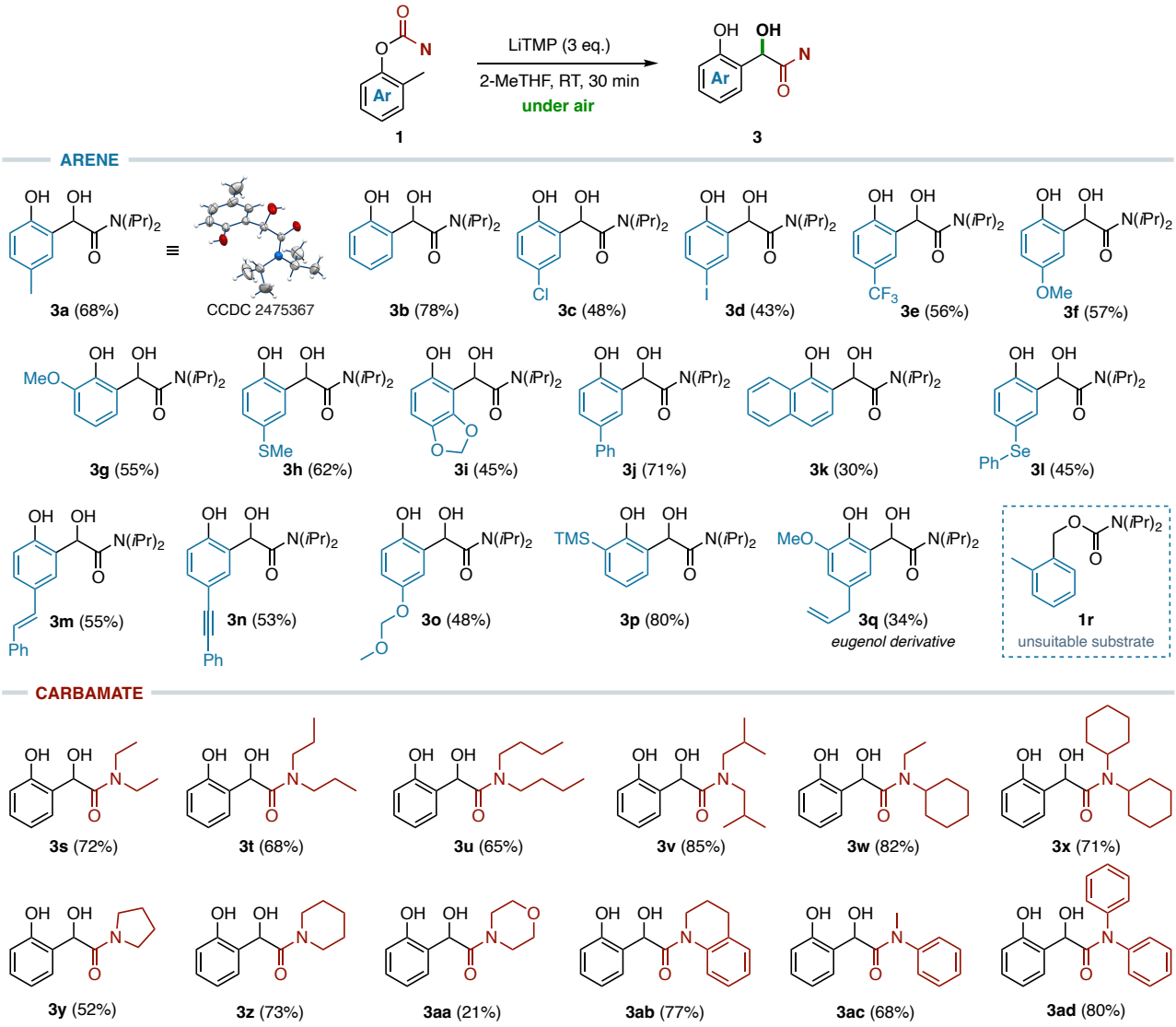


Figure S3: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **1a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mL) at RT under humidified air (82% RH). Yield **3a**: 69%.

Synthesis and analysis of α-hydroxy α-arylacetamides **3b-3ad**

General procedure. To a stirred solution of carbamate **1** (1.0 eq., 0.20 mmol) in 2-MeTHF (1 mL), LiTMP (3.0 eq., 0.60 mmol, 1 M in 2-MeTHF, 0.6 mL) was rapidly added. The resulting reaction mixture was stirred for 30 min under air and then quenched with 2 M HCl. The mixture was extracted with EtOAc (3 x 10 mL) and the combined organic layer were dried over Na_2SO_4 and concentrated under vacuum. The resulting crude reaction mixture was purified by flash column chromatography on silica gel.



2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-diisopropylacetamide (3b): General procedure starting from **1b** (0.20 mmol, 44 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 8/2 v/v) gave **3b** as a white solid (39 mg, 78%, R_f = 0.18 petroleum ether/EtOAc 8/2 v/v), mp. 184.1-187.3 °C (with dec.). ^{1}H NMR (600 MHz, CD_3OD) δ 7.17-7.09 (m, 2H), 6.87-6.80 (m, 2H), 5.64 (s, 1H), 3.97 (sept, *J* = 6.7 Hz, 1H), 3.44 (sept, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H), 0.54 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 173.2, 155.7, 130.6, 129.1, 127.4,

121.0, 116.7, 66.4, 47.3, 21.0, 20.7, 20.0, 19.0. HRMS (ESI): *m/z* calcd for $C_{14}H_{21}NO_3$ + Na^+: 274.1419 [M+Na^+]; found 274.1419.

2-(5-Chloro-2-hydroxyphenyl)-2-hydroxy-*N,N*-diisopropylacetamide (3c): General procedure starting from **1c** (0.20 mmol, 54 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v) gave **3c** as a white solid (27 mg, 48%, R_f = 0.30 petroleum ether/EtOAc 7/3 v/v), mp. 182.0-184.0 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.15-7.09 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.60 (s, 1H), 3.95 (sept, *J* = 6.6 Hz, 1H), 3.46 (sept, *J* = 6.8 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 3H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 0.63 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 172.7, 154.5, 130.2, 129.5, 128.9, 125.5, 118.0, 66.2, 47.4, 20.9, 20.7, 20.0, 19.2. HRMS (ESI): *m/z* calcd for $C_{14}H_{20}ClNO_3$ + Na^+: 308.1020 [M+Na^+]; found 308.1033.

2-Hydroxy-2-(2-hydroxy-5-iodophenyl)-*N,N*-diisopropylacetamide (3d): General procedure starting from **1d** (0.20 mmol, 72 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v) and trituration with Et_2O gave **3d** as a white solid (32 mg, 43%, R_f = 0.20 petroleum ether/EtOAc 7/3 v/v), mp. 182.0-185.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 1H), 7.34 (s, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 5.33 (s,1H), 3.79 (sept, *J* = 6.7 Hz, 1H), 3.47 (br s, 1H), 1.48 (d, *J* = 6.7 Hz, 3H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.7, 155.5, 138.7, 137.0, 127.4, 120.2, 81.9, 68.4, 48.6, 47.0, 20.9, 20.6, 19.9, 19.3. HRMS (ESI): *m/z* calcd for $C_{14}H_{20}INO_3$+ H^+: 378.0561 [M+H^+]; found 378.0572.

2-Hydroxy-2-(2-hydroxy-5-(trifluoromethyl)phenyl)-*N,N*-diisopropylacetamide (3e): General procedure starting from **1e** (0.20 mmol, 61 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v), followed by trituration with Et_2O gave **3e** as a white solid (36 mg, 56%, R_f = 0.38 petroleum ether/EtOAc 7/3 v/v), mp. 160.0-164.0 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.47-7.43 (m, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.68 (s, 1H), 3.92 (sept, *J* = 6.6 Hz, 1H), 3.46 (sept, *J* = 6.8 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.59 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 172.6, 158.9, 128.5, 127.6, 126.7, 126.7, 116.8, 66.2, 47.4, 20.9, 20.7, 19.8, 19.1. ^{19}F NMR (565 MHz, CD_3OD) δ -62.98. HRMS (ESI): *m/z* calcd for $C_{15}H_{20}F_3NO_3$ + H^+: 320.1468 [M+H^+]; found 320.1478.

2-Hydroxy-2-(2-hydroxy-5-methoxyphenyl)-*N,N*-diisopropylacetamide (3f): General procedure starting from **1f** (0.20 mmol, 53 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v) and trituration with Et_2O gave **3f** as a white solid (32 mg, 57%, R_f = 0.38 petroleum ether/EtOAc 7/3 v/v), mp. 172.0-175.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.62 (d, *J* = 3.0 Hz, 1H), 5.41 (s, 1H), 3.86 (sept, *J* = 6.6 Hz, 1H), 3.71 (s, 3H), 3.43 (sept, *J* = 6.9 Hz, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H), 0.70 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.1, 153.5, 148.6, 125.8, 118.3, 115.5, 113.1, 68.1, 55.8, 48.2, 46.6, 20.6, 20.5, 19.7, 19.1. HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_4$ + H^+: 282.1700 [M+H^+]; found 282.1709.

2-Hydroxy-2-(2-hydroxy-3-methoxyphenyl)-*N,N*-diisopropylacetamide (3g): General procedure starting from **1g** (0.20 mmol, 53 mg); purification by flash column chromatography on silica gel (petroleum

ether/EtOAc 8/2 v/v) gave **3g** as a white solid (31 mg, 55%, R_f = 0.25 petroleum ether/EtOAc 8/2 v/v), mp. 190.0-193.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84-6.76 (m, 2H), 6.74 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.99 (br s, 1H), 5.57 (s, 1H), 3.88 (s, 3H), 3.84 (sept, *J* = 6.6 Hz, 1H), 3.36 (sept, *J* = 6.9 Hz, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.38 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H), 0.52 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 171.2, 146.6, 143.1, 125.8, 120.3, 119.7, 110.3, 64.9, 56.1, 47.4, 46.2, 20.6, 20.5, 19.6, 18.6. HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_4 + Na^+$: 304.1520 [M+Na$^+$]; found 304.1528.

2-Hydroxy-2-(2-hydroxy-5-(methylthio)phenyl)-*N,N*-diisopropylacetamide (3h): General procedure starting from **1h** (0.20 mmol, 56 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v), followed by trituration with Et_2O gave **3h** as a white solid (37 mg, 62%, R_f = 0.25 petroleum ether/EtOAc 7/3 v/v), mp. 192.0-193.7 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.15 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.61 (s, 1H), 3.92 (sept, *J* = 6.6 Hz, 1H), 3.45 (sept, *J* = 6.8 Hz, 1H), 2.36 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.36 (d, *J* = 6.8, Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H), 0.57 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 173.0, 154.4, 131.7, 130.1, 129.4, 128.4, 117.4, 66.3, 48.9, 47.4, 20.9, 20.7, 20.0, 19.1, 18.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_3S + H^+$: 298.1471 [M+H$^+$]; found 298.1482.

2-Hydroxy-2-(5-hydroxybenzo[d][1,3]dioxol-4-yl)-*N,N*-diisopropylacetamide (3i): General procedure starting from **1i** (0.20 mmol, 56 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v) and trituration with Et_2O gave **3i** as a white solid (27 mg, 45%, R_f = 0.23 petroleum ether/EtOAc 7/3 v/v), mp. 189.0-191.0 °C (with dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.43 (br s, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 5.93 (s, 1H), 5.75 (s, 1H), 5.27 (d, *J* = 4.9 Hz, 1H), 4.94 (d, *J* = 5.1 Hz, 1H), 3.69 (sept, *J* = 6.7 Hz, 1H), 3.41 (sept, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.51 (d, *J* = 6.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 170.0, 149.9, 145.7, 139.7,111.0, 107.7, 106.3, 100.8, 62.4, 47.0, 45.3, 20.6, 20.3, 19.5, 18.3. HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NO_5 + Na^+$: 318.1317 [M+Na$^+$]; found 318.1320.

2-Hydroxy-2-(4-hydroxy-[1,1'-biphenyl]-3-yl)-*N,N*-diisopropylacetamide (3j): General procedure starting from **1j** (0.20 mmol, 62 mg); purification by trituration with Et_2O gave **3j** as a white solid (46 mg, 71%), mp. 192.0-193.8 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.51-7.48 (m, 2H), 7.43 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.70 (s, 1H), 4.00 (sept, *J* = 6.6 Hz, 1H), 3.46 (sept, *J* = 6.8 Hz, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.58 (d, *J* = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 173.2, 155.3, 142.0, 134.3, 129.8, 129.1, 127.8, 127.7, 127.6, 127.3, 117.1, 66.5, 47.4, 21.0, 20.7, 20.0, 19.1. HRMS (ESI): *m/z* calcd for $C_{20}H_{25}NO_3 + H^+$: 328.1907 [M+H$^+$]; found 328.1919.

2-Hydroxy-2-(1-hydroxynaphthalen-2-yl)-*N,N*-diisopropylacetamide (3k): General procedure starting from **1k** (0.20 mmol, 57 mg); purification by flash column chromatography on silica gel (DCM/MeOH 95/5 v/v) and trituration with Et_2O gave **3k** as a white solid (18 mg, 30%, R_f = 0.30 DCM/MeOH 95/5 v/v), mp. 163.3-168.2 °C (with dec.). ^{1}H NMR (400 MHz, THF-d_8) δ 8.97 (br s, 1H), 8.22 (m, 1H), 7.72 (m, 1H), 7.41

(dt, J = 6.4, 3.4 Hz, 2H), 7.34 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 5.66 (d, J = 4.9 Hz, 1H), 5.15 (d, J = 5.5 Hz, 1H), 4.19 (sept, J = 6.6 Hz, 1H), 3.41 (sept, J = 6.8 Hz, 1H), 1.44 (d, J = 6.8 Hz, 3H), 1.35 (d, J = 6.7 Hz, 3H), 1.12 (d, J = 6.7 Hz, 3H), 0.55 (d, J = 6.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ 173.2, 151.5, 135.5, 128.4, 127.2, 127.0, 126.2, 125.8, 123.3, 121.7, 120.8, 69.2, 48.6, 47.2, 21.1, 20.9, 20.3, 19.6. HRMS (ESI): *m/z* calcd for $C_{18}H_{23}NO_3 + Na^+$: 324.1576 [M+Na^+]; found 324.1581.

2-Hydroxy-2-(2-hydroxy-5-(phenylselanyl)phenyl)-*N,N*-diisopropylacetamide (3l): General procedure starting from **1l** (0.20 mmol, 0.81 g) and LiTMP (3.0 eq., 1 M in 2-MeTHF) in 2-MeTHF (1 mL); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v) and trituration with Et_2O gave **3l** as a white solid (37 mg, 45%, R_f = 0.20 petroleum ether/EtOAc 7/3 v/v), mp. 179.0-182.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.3, 2.1 Hz, 1H), 7.33-7.30 (m, 3H), 7.22-7.15 (m, 3H), 6.83 (d, J = 8.3 Hz, 1H), 5.32 (s, 1H), 3.81 (sept, J = 6.5 Hz, 1H), 3.42 (sept, J = 6.7 Hz, 1H), 1.45 (d, J = 6.8 Hz, 3H), 1.35 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.7 Hz, 3H), 0.67 (d, J = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 171.0, 156.0, 137.2, 135.8, 133.0, 131.4, 129.3, 126.8, 125.9, 119.9, 119.1, 69.3, 48.6, 47.0, 20.8, 20.6, 19.9, 19.3. HRMS (ESI): *m/z* calcd for $C_{20}H_{25}NO_3Se + Na^+$: 430.0897 [M+$Na^+$]; found 430.0901.

(*E*)-2-Hydroxy-2-(2-hydroxy-5-styrylphenyl)-*N,N*-diisopropylacetamide (3m): General procedure starting from **1m** (0.20 mmol, 67 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 7/3 v/v) and trituration with Et_2O gave **3m** as a white solid (39 mg, 55%, R_f = 0.30 petroleum ether/EtOAc 7/3 v/v), mp. 195.0-200.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.37-7.31 (m, 3H), 7.25-7.21 (m, 2H), 6.99 (d, J = 16.3 Hz, 1H), 6.91 (d, J = 16.3 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.46 (s, 1H), 3.89 (sept, J = 6.7 Hz, 1H), 3.47 (sept, J = 6.4 Hz, 1H), 1.50 (d, J = 6.8 Hz, 3H), 1.47 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 6.7 Hz, 3H), 0.72 (d, J = 6.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 171.2, 154.8, 137.4, 130.0, 128.7, 128.0, 127.8, 127.3, 126.7, 126.6, 126.2, 125.0, 117.9, 68.6, 48.4, 46.8, 20.7, 20.5, 19.8, 19.1. HRMS (ESI): *m/z* calcd for $C_{22}H_{27}NO_3 + Na^+$: 376.1889 [M+Na^+]; found 376.1896.

2-Hydroxy-2-(2-hydroxy-5-(phenylethynyl)phenyl)-*N,N*-diisopropylacetamide (3n): General procedure starting from **1n** (0.20 mmol, 67 mg); purification by trituration with Et_2O gave **3n** as a white solid (37 mg, 53%), 194.0-198.1 °C (with dec.). ^1H NMR (400 MHz, THF-d_8) δ 9.14 (br s, 1H), 7.44 (dd, J = 7.7, 1.8 Hz, 2H), 7.36-7.22 (m, 5H), 6.78 (d, J = 8.2 Hz, 1H), 5.49 (d, J = 5.1 Hz, 1H), 4.97 (d, J = 5.9 Hz, 1H), 4.02 (sept, J = 6.6 Hz, 1H), 3.40 (sept, J = 6.7 Hz, 1H), 1.44 (d, J = 6.7 Hz, 3H), 1.36 (d, J = 6.7 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H), 0.60 (d, J = 6.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ 172.8, 156.0, 133.2, 132.7, 132.2, 129.3, 129.2, 128.7, 125.0, 116.9, 115.8, 90.4, 88.3, 66.2, 48.2, 47.0, 21.1, 20.9, 20.1, 19.5. HRMS (ESI): *m/z* calcd for $C_{22}H_{25}NO_3 + Na^+$: 374.1732 [M+Na^+]; found 376. 1732.

2-Hydroxy-2-(2-hydroxy-5-(methoxymethoxy)phenyl)-*N,N*-diisopropylacetamide (3o): General procedure starting from **1o** (0.20 mmol, 59 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 6/4 v/v) and trituration with Et_2O gave **3o** as a white solid (30 mg, 48%, R_f = 0.30 petroleum ether/EtOAc 6/4 v/v), mp. 155.0-157-0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 6.88 (dd, J = 8.8, 2.9 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.79 (d, J = 2.9 Hz, 1H), 5.35 (s, 1H), 5.06 (q, J = 6.8 Hz, 2H), 3.86 (sept, J =

6.7 Hz, 1H), 3.50-3.44 (m, 1H) superimposed to 3.43 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 170.9, 151.0, 150.1, 125.4, 118.4, 116.2, 95.2, 68.9, 55.7, 48.4, 46.8, 20.7, 20.5, 19.7, 19.1. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_5 + H^+$: 312.1812 [M+H$^+$]; found 312.1813.

2-Hydroxy-2-(2-hydroxy-3-(trimethylsilyl)phenyl)-*N,N*-diisopropylacetamide (3p): General procedure starting from **1p** (0.20 mmol, 62 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 9/1 v/v) gave **3p** as a white solid (52 mg, 80%, R_f = 0.18 petroleum ether/EtOAc 9/1 v/v), mp. 92.0-95.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.28 (s, 1H), 4.62 (br s, 1H), 3.84 (sept, *J* = 6.6 Hz, 1H), 3.51-3.39 (m, 1H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 0.70 (d, *J* = 6.6 Hz, 3H), 0.27 (s, 9H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.2, 160.7, 135.4, 129.9, 128.3, 123.1, 119.9, 70.7, 48.6, 46.8, 20.7, 20.5, 19.7, 19.1, -1.1. HRMS (ESI): *m/z* calcd for $C_{17}H_{29}NO_3Si + H^+$: 324.1989 [M+H$^+$]; found 324.1999.

2-(5-Allyl-2-hydroxy-3-methoxyphenyl)-2-hydroxy-*N,N*-diisopropylacetamide (3q): General procedure starting from **1q** (0.20 mmol, 61 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 9/1 v/v) gave **3q** as a yellow solid (22 mg, 34%, R_f = 0.16 petroleum ether/acetone 9/1 v/v), mp. 142.0-144.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 (d, *J* = 1.9 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 5.91-5.84 (m, 1H), 5.83-5.81 (m, 1H), 5.55 (d, *J* = 6.0 Hz, 1H), 5.03-5.00 (m, 1H), 4.99 (t, *J* = 1.4 Hz, 1H), 4.96 (d, *J* = 6.0 Hz, 1H), 3.87 (s, 3H), 3.81 (sept, *J* = 6.6 Hz, 1H), 3.35 (sept, *J* = 6.8 Hz, 1H), 3.30-3.21 (m, 2H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H), 0.52 (d, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.45, 146.70, 141.50, 137.68, 132.14, 125.61, 119.63, 115.70, 110.97, 65.08, 56.28, 47.59, 46.38, 40.02, 20.79, 20.74, 19.68, 18.76. HRMS (ESI): *m/z* calcd for $C_{18}H_{27}NO_4 + H^+$: 322.2022 [M+H$^+$]; found 322.2021.

2-Hydroxy-*N,N*-diisopropyl-2-(o-tolyl)acetamide (3r): General procedure starting from **1r** (0.20 mmol, 50 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 95/5 v/v) gave **3r** as a white semisolid (44 mg, 88%, R_f = 0.18 petroleum ether/EtOAc 95/5 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.14 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 1H), 5.26 (d, *J* = 5.6 Hz, 1H), 4.95 (d, *J* = 5.6 Hz, 1H), 3.54 (sept, *J* = 6.7 Hz, 1H), 3.38 (sept, *J* = 6.8 Hz, 1H), 2.46 (s, 3H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.4, 138.2, 136.2, 131.2, 128.5, 127.2, 126.7, 69.1, 48.1, 46.5, 20.7, 20.7, 19.9, 19.2, 18.7. HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_2 + H^+$: 250.1802 [M+H$^+$]; found 250.1800.

2-Hydroxy-2-(2-hydroxyphenyl)-*N,N*-diethylacetamide (3s): General procedure starting from **1s** (0.20 mmol, 41 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 6/4 v/v) gave **3s** as a white solid (32 mg, 72%, R_f = 0.28 petroleum ether/EtOAc 6/4 v/v) mp. 111.0-113.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (br s, 1H), 7.18 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.85 (td, *J* = 7.5, 1.1 Hz, 1H), 5.46 (s, 1H), 4.54 (br s, 1H), 3.51 (m, 1H), 3.39 (m, 1H), 3.25 (quint, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz,

$CDCl_3$) δ 172.1, 155.6, 130.3, 128.5, 124.6, 120.6, 117.8, 68.8, 41.6, 41.2, 13.6, 12.8. HRMS (ESI): *m/z* calcd for $C_{12}H_{17}NO_3 + H^+$: 224.1292 [M+H$^+$]; found 224.1287.

2-Hydroxy-2-(2-hydroxyphenyl)-*N,N*-dipropylacetamide (3t): General procedure starting from **1t** (0.20 mmol, 47 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 8/2 v/v) gave **3t** as a white solid (34 mg, 68%, R_f = 0.18 petroleum ether/acetone 8/2 v/v), mp. 113.0-114.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.06 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.88-6.83 (m, 2H), 5.47 (s, 1H), 4.53 (br s, 1H), 3.49 (ddd, *J* = 13.3, 9.1, 6.4 Hz, 1H), 3.22 (ddd, *J* = 13.3, 9.1, 6.3 Hz, 1H), 3.15 (ddd, *J* = 14.6, 10.2, 6.0 Hz, 1H), 3.03 (ddd, *J* = 14.9, 10.3, 5.1 Hz, 1H), 1.64-1.55 (m, 2H) superimposed to 1.54-1.47 (m, 1H), 1.32-1.18 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 172.6, 155.5, 130.3, 128.6, 124.7, 120.6, 117.8, 68.8, 48.9, 48.4, 21.7, 20.7, 11.4, 11.1. HRMS (ESI): *m/z* calcd for $C_{14}H_{21}NO_3 + H^+$: 252.1594 [M+H$^+$]; found 252.1597.

2-Hydroxy-2-(2-hydroxyphenyl)-*N,N*-dibutylacetamide (3u): General procedure starting from **1u** (0.20 mmol, 53 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 85/15 v/v) gave **3u** as a white solid (36 mg, 65%, R_f = 0.24 petroleum ether/acetone 85/15 v/v), mp. 93.2-95.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.91-6.80 (m, 2H), 5.45 (s, 1H), 4.48 (br s, 1H), 3.50 (ddd, *J* = 13.3, 9.5, 6.0 Hz, 1H), 3.26 (ddd, *J* = 13.3, 9.5, 5.9 Hz, 1H), 3.18 (ddd, *J* = 15.2, 9.8, 5.7 Hz, 1H), 3.05 (ddd, *J* = 14.7, 10.5, 4.3 Hz, 1H), 1.60-1.49 (m, 2H), 1.48-1.40 (m, 1H), 1.30 (sext, *J* = 7.8 Hz, 2H), 1.23-1.14 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 172.5, 155.6, 130.3, 128.7, 124.6, 120.6, 117.9, 69.0, 47.2, 46.7, 30.6, 29.6, 20.3, 20.1, 13.9, 13.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_3 + H^+$: 280.1907 [M+H$^+$]; found 280.1911.

2-Hydroxy-2-(2-hydroxyphenyl)-*N,N*-diisobutylacetamide (3v): General procedure starting from **1v** (0.20 mmol, 53 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 85/15 v/v) gave **3v** as a white solid (47 mg, 85%, R_f = 0.20 petroleum ether/acetone 85/15 v/v), mp. 139.2-140.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br s, 1H), 7.13 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.85-6.77 (m, 2H), 5.58 (s, 1H), 4.64 (br s, 1H), δ 3.69 (ddd, *J* = 13.4, 7.7, 0.9 Hz, 1H), 3.16 (ddd, *J* = 14.6, 8.4, 0.9 Hz, 1H), 2.84 (dd, *J* = 13.4, 7.6 Hz, 1H), 2.77 (dd, *J* = 14.6, 6.9 Hz, 1H), 1.99 (non, *J* = 6.5 Hz, 1H) superimposed to 1.90 (non, *J* = 6.6 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.83-0.77 (m, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 173.7, 155.1, 130.2, 128.7, 124.8, 120.5, 117.5, 68.1, 54.1, 53.6, 27.4, 26.4, 20.3, 20.0, 20.0, 19.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_3 + H^+$: 280.1914 [M+H$^+$]; found 280.1914.

2-Hydroxy-2-(2-hydroxyphenyl)-*N*-cyclohexyl-*N*'-ethyl-acetamide (3w): General procedure starting from **1w** (0.20 mmol, 52 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 8/2 v/v) gave **3w** as a white solid (45 mg, 82%, R_f = 0.20 petroleum ether/acetone 8/2 v/v), mp. 152.0-153.0 °C. Mixture of stereoisomers (7:3 ratio). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23-7.16 (m, 1H), 7.12-7.09 (m, 1H major), 7.03 (dd, *J* = 7.6, 1.7 Hz, 1H minor), 6.93-6.82 (m, 2H), 5.47 (s, 1H major), 5.38 (s, 1H minor), 4.68 (br s, 1H major), 4.31 (br s, 1H minor), 4.23 (tt, *J* = 12.1, 3.6 Hz, 1H minor), 3.49 (tt, *J* = 11.7, 3.6 Hz, 1H major), 3.42-3.29 (m, 2H major), 3.27-3.16 (m, 2H minor), 1.87-1.78 (m, 2H) superimposed to 1.77-1.62 (m,

2H) superimposed to 1.61-1.54 (m, 2H) superimposed to 1.53-1.44 (m, 1H), 1.43-1.33 (m, 1H) superimposed to 1.32-1.22 (m, 1H) superimposed to 1.21-1.17 (m, 2H), 1.11 (t, J = 7.2 Hz, 1H), 1.05-0.84 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.0, 155.2, 130.4, 130.2, 128.8, 128.6, 124.9, 124.4, 120.7, 120.5, 118.2, 117.7, 70.2, 69.1, 56.5, 56.3, 38.5, 37.8, 31.7, 30.7, 30.6, 26.0, 25.9, 25.9, 25.6, 25.6, 25.2, 16.3, 14.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{23}NO_3 + H^+$: 278.1751 [M+H$^+$]; found 278.1758.

2-Hydroxy-2-(2-hydroxyphenyl)-*N,N*-dicyclohexylacetamide (3x): General procedure starting from **1x** (0.20 mmol, 63 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 85/15 v/v) gave **3x** as a white solid (47 mg, 71%, R_f = 0.34 petroleum ether/acetone 85/15 v/v), mp. 172.0-174.0 °C. Mixtures of stereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (ddd, J = 8.0, 7.3, 1.6 Hz, 1H), 7.09 (dd, J = 7.6, 1.7 Hz, 1H), 6.84 (td, J = 7.5, 1.1 Hz, 1H) superimposed to 6.81 (dd, J = 8.1, 1.2 Hz, 1H), 5.42 (s, 1H), 4.91 (br s, 1H), 3.42 (tt, J = 11.7, 3.6 Hz, 1H), 2.98-2.87 (m, 1H), 2.57-2.44 (m, 2H), 1.85-1.75 (m, 3H) superimposed to 1.71 (d, J = 12.6 Hz, 1H), 1.64-1.59 (m, 1H) superimposed to 1.58-1.52 (m, 2H) superimposed to 1.52-1.44 (m, 2H) superimposed to 1.43-1.37 (m, 1H), 1.32-1.10 (m, 5H), 1.03-0.93 (m, 1H), 0.92-0.81 (m, 1H), 0.68 (d, J = 12.2 Hz, 1H).$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.9, 154.9, 123.0, 128.8, 125.3, 120.6, 117.5, 68.8, 56.9, 31.1, 30.0, 29.7, 29.1, 26.6, 26.5, 25.9, 25.4, 25.4, 25.2. HRMS (ESI): *m/z* calcd for $C_{20}H_{29}NO_3 + H^+$: 332.2231 [M+H$^+$]; found 332.2228.

2-Hydroxy-2-(2-hydroxyphenyl)-1-(pyrrolidin-1-yl)ethan-1-one (3y): General procedure starting from **1y** (0.20 mmol, 41 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 1/1 v/v) gave **3y** as a colourless oil (24 mg, 52%, R_f = 0.13 petroleum ether/EtOAc 1/1 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (br s, 1H), 7.21 (ddd, J = 8.1, 7.3, 1.7 Hz, 1H), 7.09 (dd, J = 7.6, 1.7 Hz, 1H), 6.92 (dd, J = 8.1, 1.2 Hz, 1H), 6.85 (td, J = 7.4, 1.2 Hz, 1H), 5.32 (s, 1H), 4.25 (br s, 1H), 3.60 (dt, J = 13.0, 6.8 Hz, 1H), 3.56-3.48 (m, 2H), 3.14 (dt, J = 10.5, 6.6 Hz, 1H), 1.97-1.77 (m, 4H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.2, 156.1, 130.4, 129.2, 123.5, 120.4, 118.1, 71.3, 46.9, 46.3, 26.0, 24.0. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}NO_3 + H^+$: 222.1236 [M+H$^+$]; found 222.1231.

2-Hydroxy-2-(2-hydroxyphenyl)-1-(piperidin-1-yl)ethan-1-one (3z): General procedure starting from **1z** (0.20 mmol, 44 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 8/2 v/v) gave **3z** as a colourless oil (34 mg, 73%, R_f = 0.15 petroleum ether/acetone 8/2 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 7.06 (dd, J = 7.6, 1.7 Hz, 1H), 6.90-6.82 (m, 2H), 5.53 (s, 1H), 4.69 (br s, 1H), 3.80-3.68 (m, 1H), 3.58-3.47 (m, 1H), 3.29-3.21 (br m, 2H), 1.60-1.52 (m, 3H) superimposed to 1.53-1.48 (br m, 1H),1.44-1.35 (br m, 1H), 1.14-1.03 (br m, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 170.9, 155.2, 130.1, 128.3, 124.7, 120.6, 117.6, 68.0, 46.2, 44.9, 44.3, 25.6, 24.3. HRMS (ESI): *m/z* calcd for $C_{13}H_{17}NO_3 + H^+$: 236.1294 [M+H$^+$]; found 236.1287.

2-Hydroxy-2-(2-hydroxyphenyl)-1-morpholinoethan-1-one (3aa): General procedure starting from **1aa** (0.20 mmol, 44 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 7/3 v/v) gave **3aa** as a yellow oil (10 mg, 21%, R_f = 0.31 petroleum ether/acetone 7/3 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 7.08 (dd, J = 7.6, 1.7 Hz, 1H), 6.90-6.85 (m, 2H), 5.54 (s, 1H),

3.86-3.48 (m, 4H), 3.42-3.35 (m, 1H), 3.32-3.19 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5, 154.8, 130.4, 128.1, 124.4, 121.0, 117.6, 67.9, 66.7, 66.2, 45.5, 43.4. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}NO_4 + H^+$: 238.1085 [$M+H^+$]; found 238.1081.

1-(3,4-Dihydroquinolin-1(2*H*)-yl)-2-hydroxy-2-(2-hydroxyphenyl)ethan-1-one (3ab): General procedure starting from **1ab** (0.20 mmol, 53 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 8/2 v/v) gave **3ab** as a colourless oil (44 mg, 77%, R_f = 0.24 petroleum ether/acetone 8/2 v/v). Mixture of stereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.08 (m, 6H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.83-6.50 (m, 1H), 5.68 (s, 1H), 4.14-3.71 (m, 2H), 3.68-3.53 (m, 1H), 2.70-2.56 (m, 1H), 2.44-2.23 (m, 1H), 2.01-1.87 (m, 1H), 1.85-1.70 (m, 1H), 1.66-1.49 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 174.0, 154.5, 137.7, 131.0, 130.0, 129.7, 128.7, 127.4, 127.2, 126.2, 125.2, 124.9, 124.8, 124.7, 121.7, 120.2, 118.5, 117.9, 117.5, 111.6, 111.5, 111.4, 70.5, 68.1, 42.8, 42.4, 27.9, 26.3, 22.5, 21.2. HRMS (ESI): *m/z* calcd for $C_{17}H_{17}NO_3 + H^+$: 284.1289 [$M+H^+$]; found 284.1289.

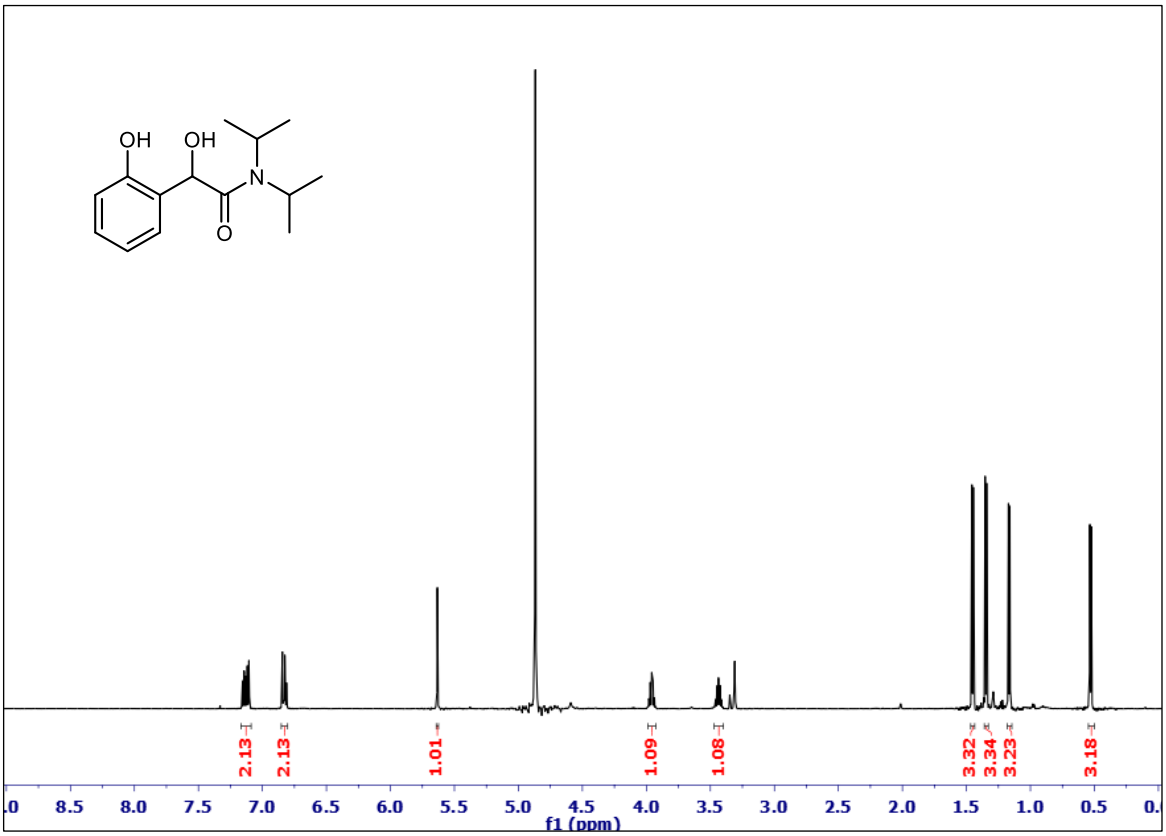
2-Hydroxy-2-(2-hydroxyphenyl)-*N*-methyl-*N*'-phenylacetamide (3ac): General procedure starting from **1ac** (0.20 mmol, 48 mg); purification by flash column chromatography on silica gel (petroleum ether/acetone 8/2 v/v) gave **3ac** as a white solid (35 mg, 68%, R_f = 0.18 petroleum ether/acetone 8/2 v/v), mp. 98.0-99.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 7.42-7.35 (m, 3H), 7.15 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 7.07-7.03 (m, 2H), 6.87 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.66 (td, *J* = 7.4, 1.2 Hz, 1H), 6.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.08 (s, 1H), 3.34 (s, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 173.6, 156.3, 141.8, 130.4, 130.1, 130.0, 129.0, 127.6, 123.7, 120.1, 118.5, 71.8, 38.5. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}NO_3 + H^+$: 258.1141 [$M+H^+$]; found 258.1133.

2-Hydroxy-2-(2-hydroxyphenyl)-*N,N*-diphenylacetamide (3ad): General procedure starting from **1ad** (0.20 mmol, 61 mg); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 6/4 v/v) gave **3ad** as a white solid (51 mg, 80%, R_f = 0.30 petroleum ether/EtOAc 6/4 v/v), mp. 159.8-162.0 °C (with dec.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.37-7.31 (m, 5H), 7.25 (br s, 3H), 7.17 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H), 7.13-7.05 (m, 2H), 6.87 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.68 (td, *J* = 7.5, 1.2 Hz, 1H), 6.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.32 (s, 1H), 3.96 (s, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 173.9, 155.9, 130.4, 130.1, 130.0, 129.3, 128.8, 127.2, 126.2, 123.6, 120.4, 118.2, 72.0. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}NO_3 + H^+$: 320.1292 [$M+H^+$]; found 320.1292.

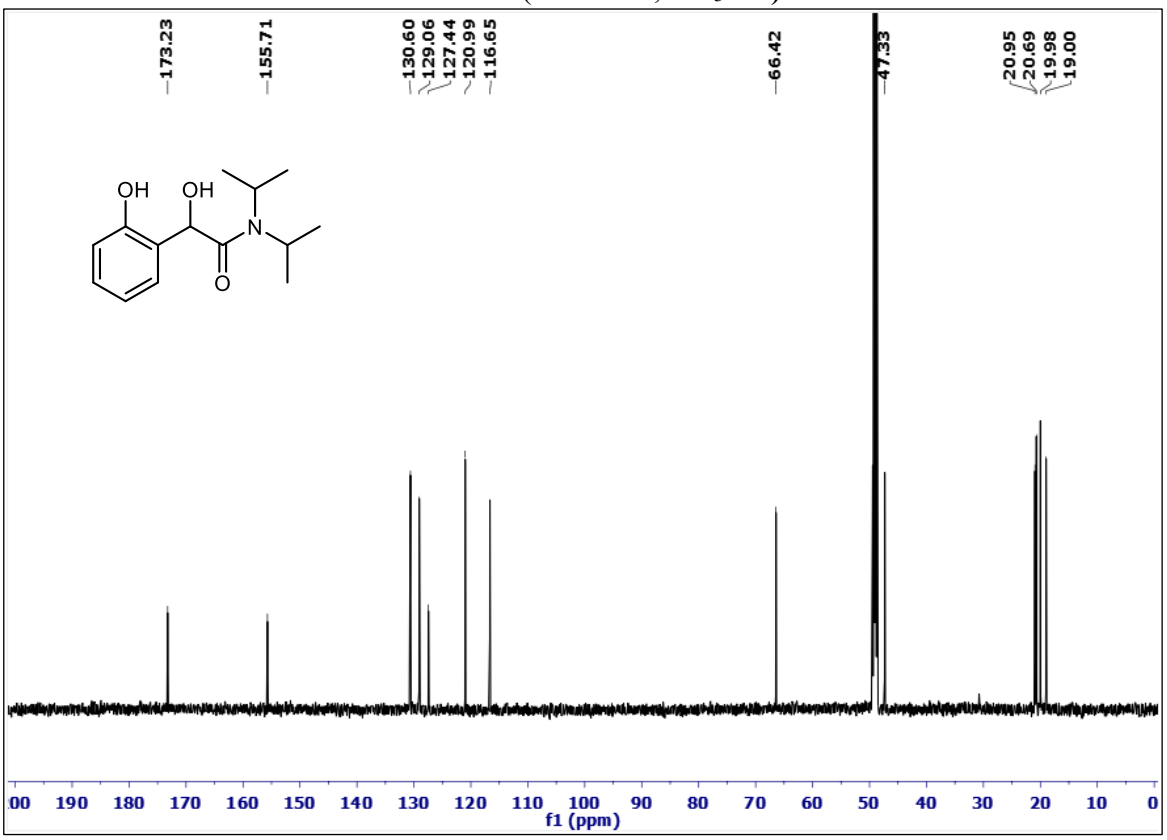
^{1}H and ^{13}C NMR spectra of compounds **3**

2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-diisopropylacetamide (3b)

^{1}H NMR (600 MHz, CD_3OD)

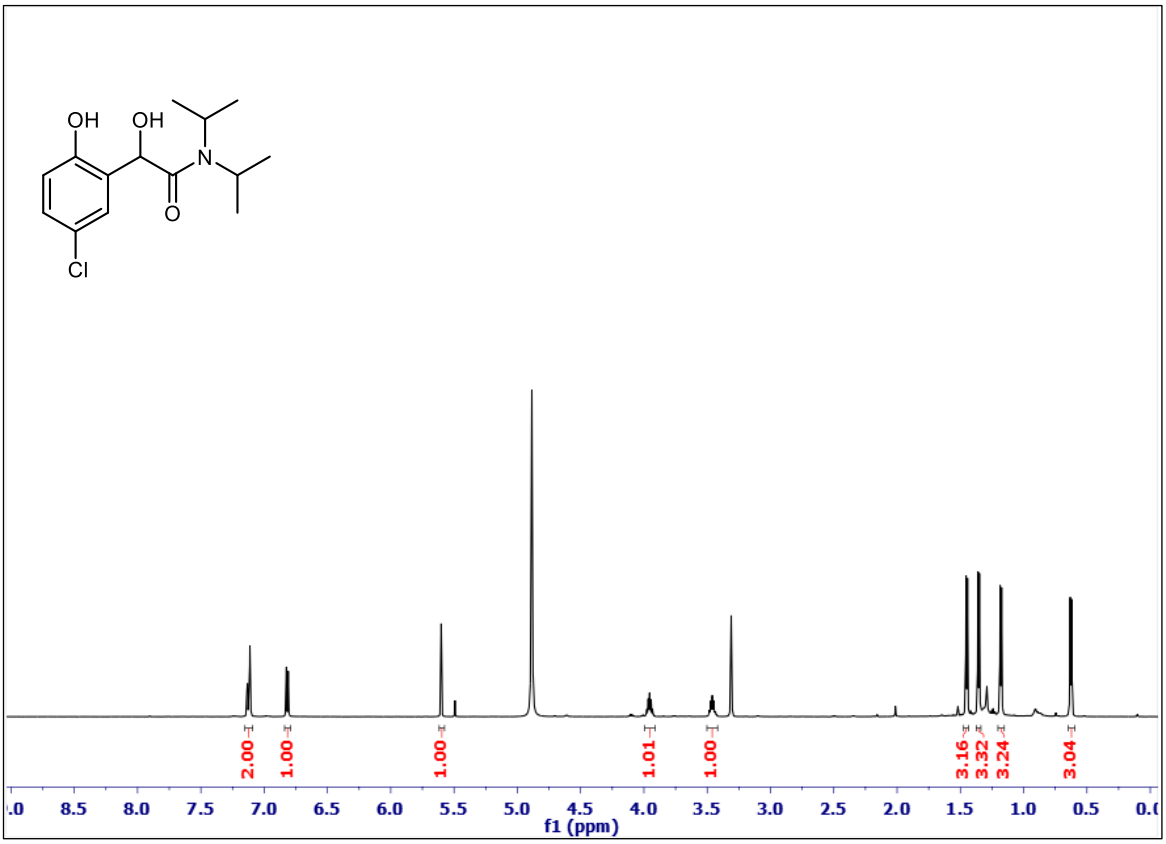


^{13}C NMR (150 MHz, CD_3OD)

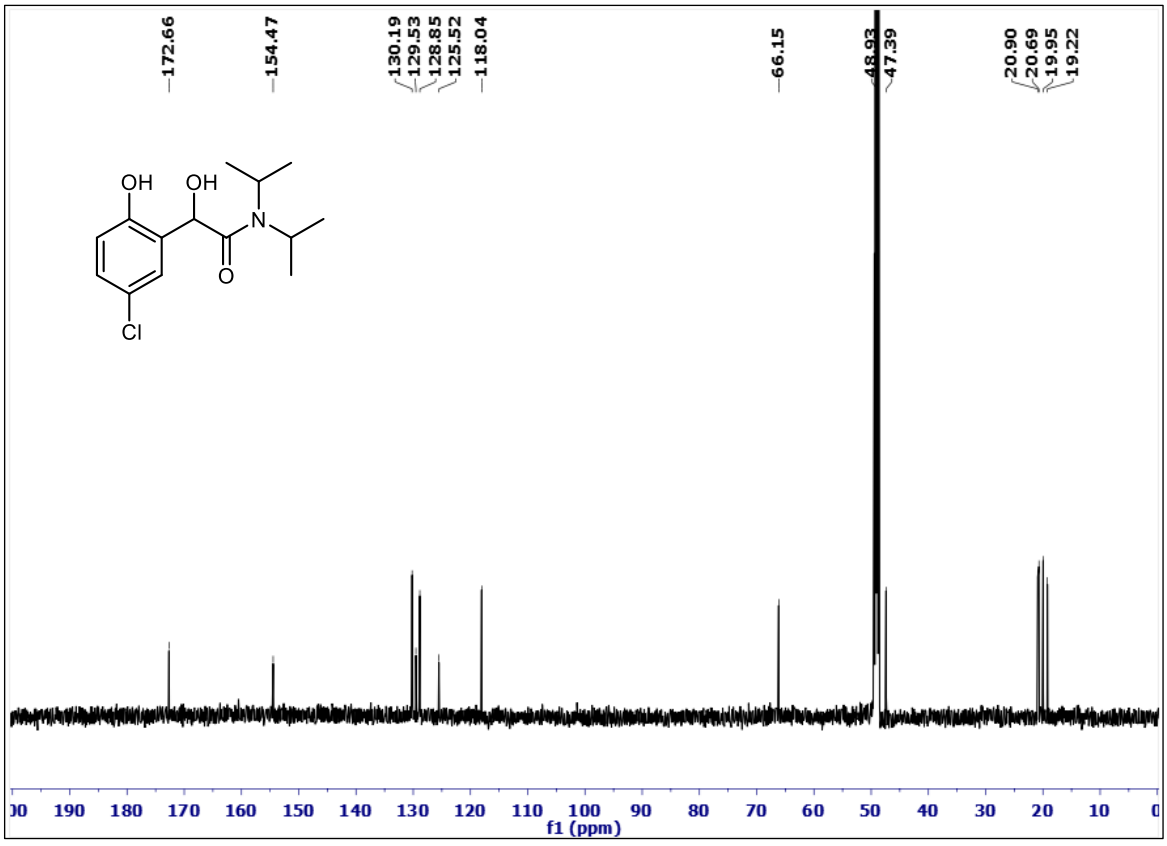


2-(5-Chloro-2-hydroxyphenyl)-2-hydroxy-*N*,*N*-diisopropylacetamide (3c)

^{1}H NMR (600 MHz, CD_3OD)

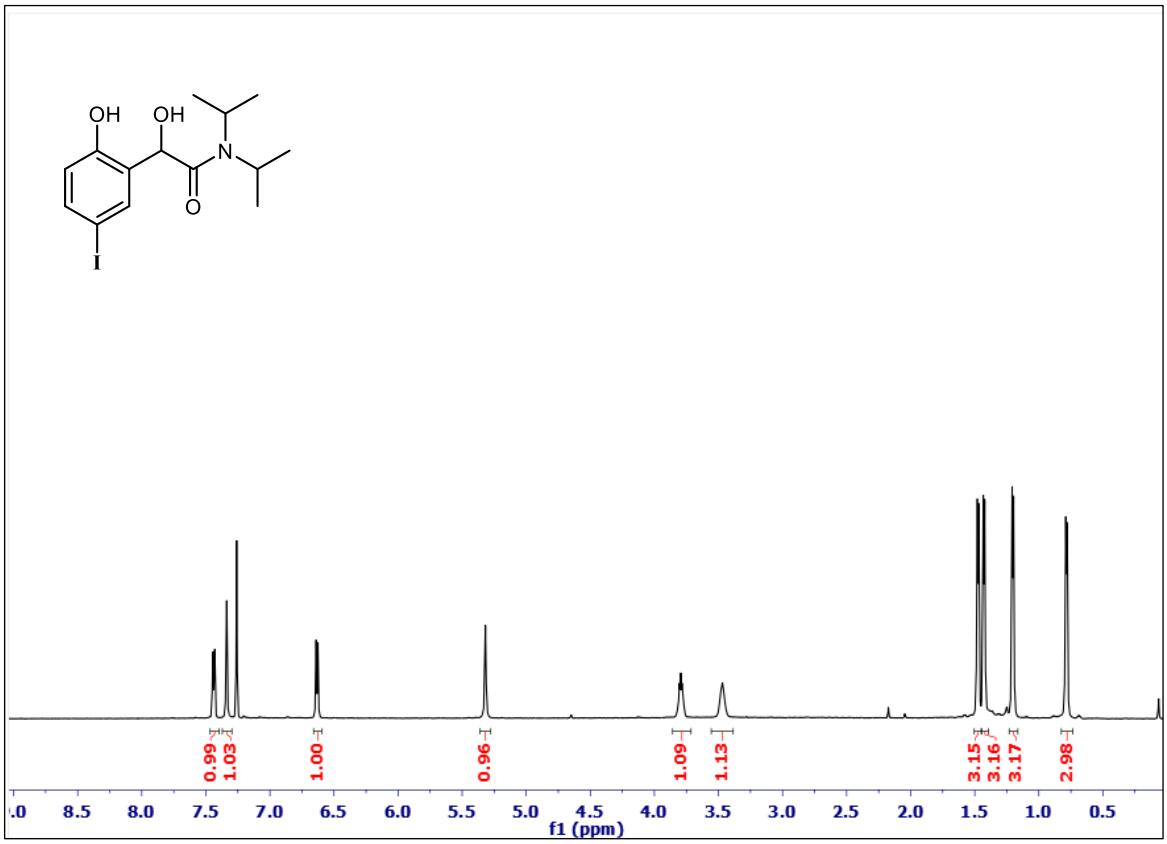


^{13}C NMR (150 MHz, CD_3OD)

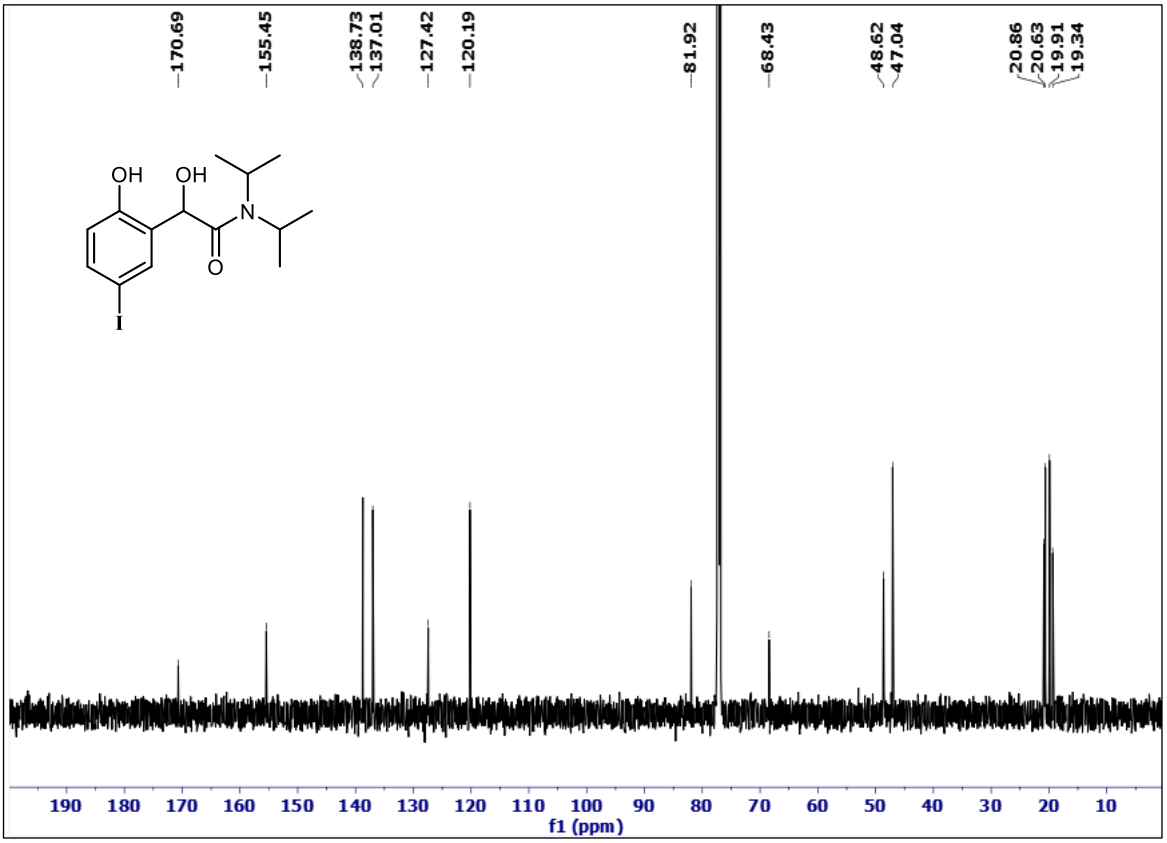


2-Hydroxy-2-(2-hydroxy-5-iodophenyl)-*N*,*N*-diisopropylacetamide (3d)

^{1}H NMR (600 MHz, $CDCl_3$)

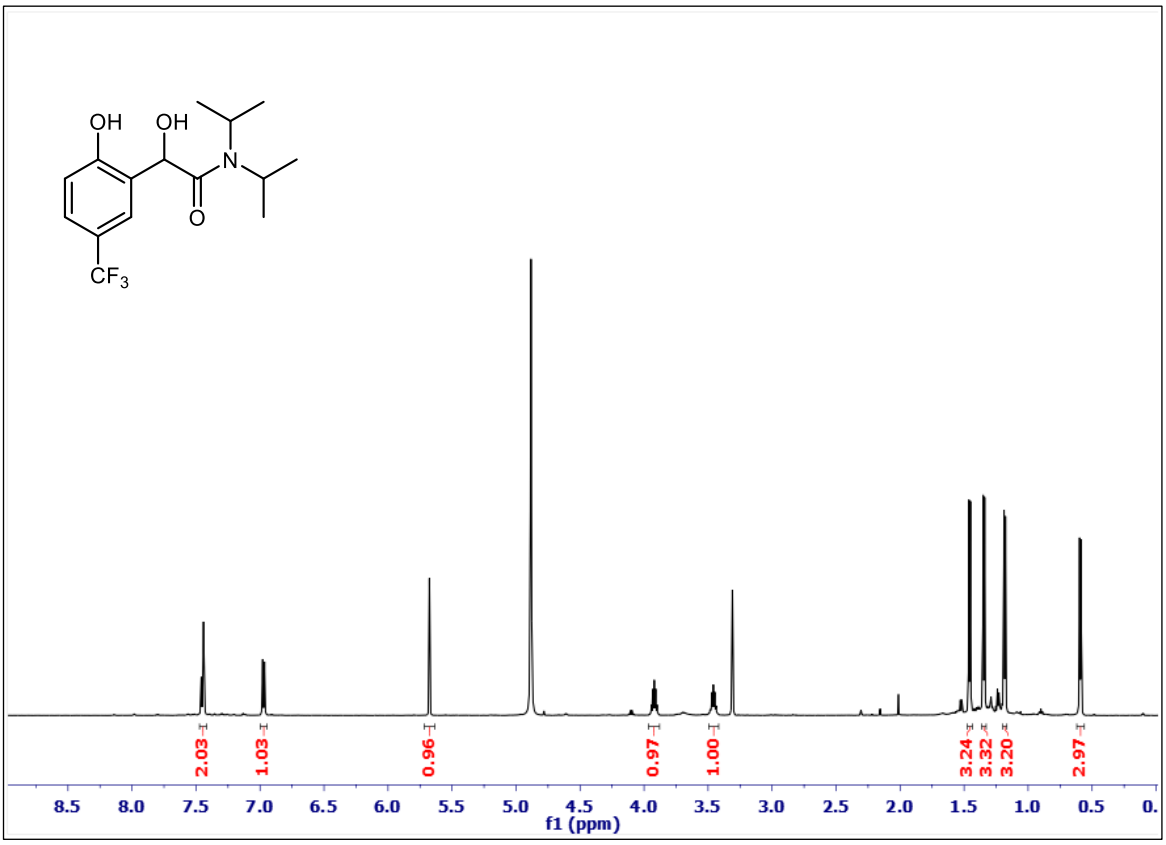


^{13}C NMR (150 MHz, $CDCl_3$)

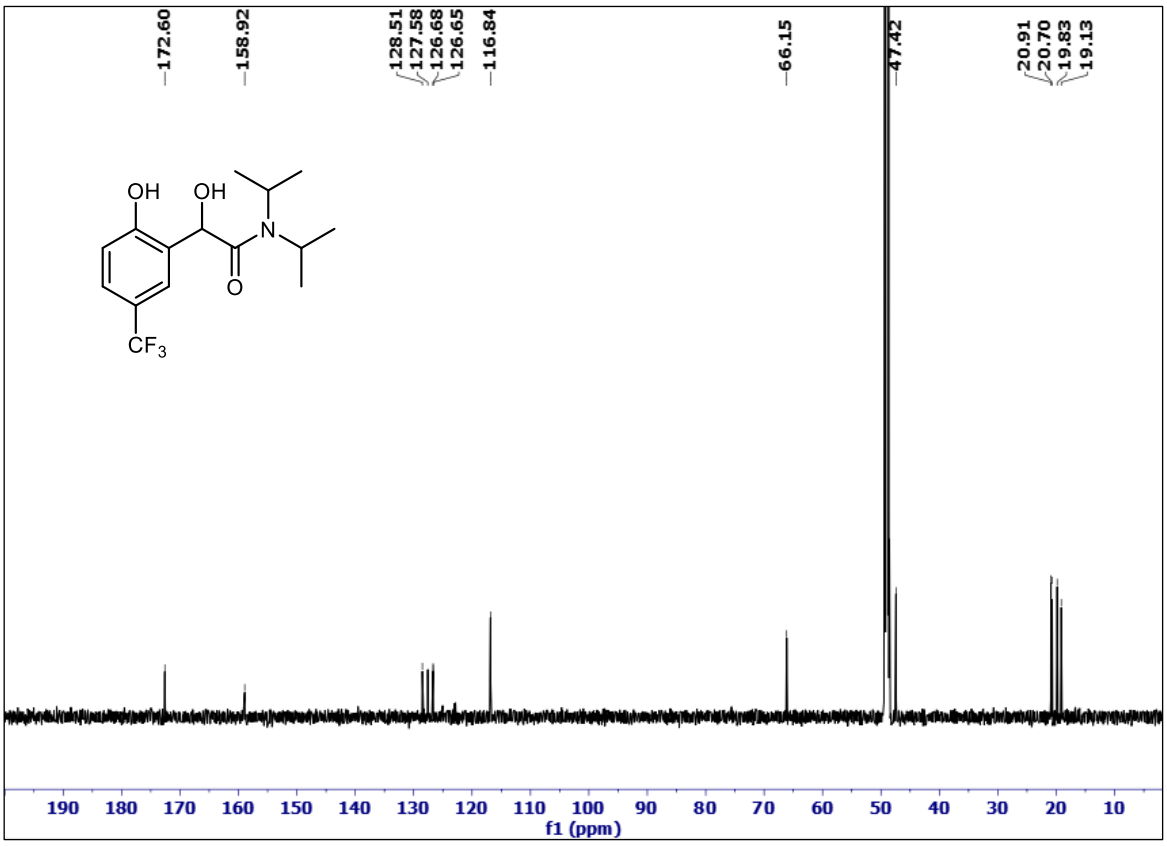


2-Hydroxy-2-(2-hydroxy-5-(trifluoromethyl)phenyl)-*N*,*N*-diisopropylacetamide (3e)

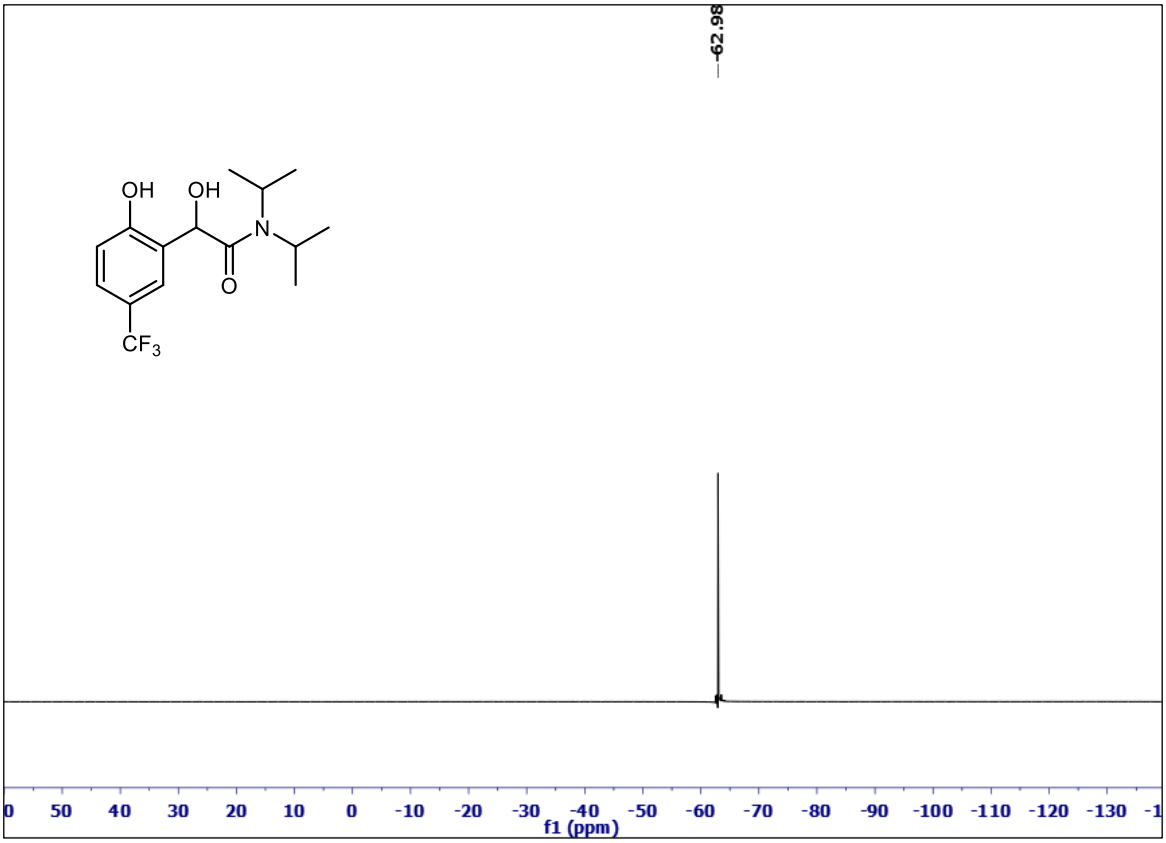
^{1}H NMR (600 MHz, CD_3OD)



^{13}C NMR (150 MHz, CD_3OD)

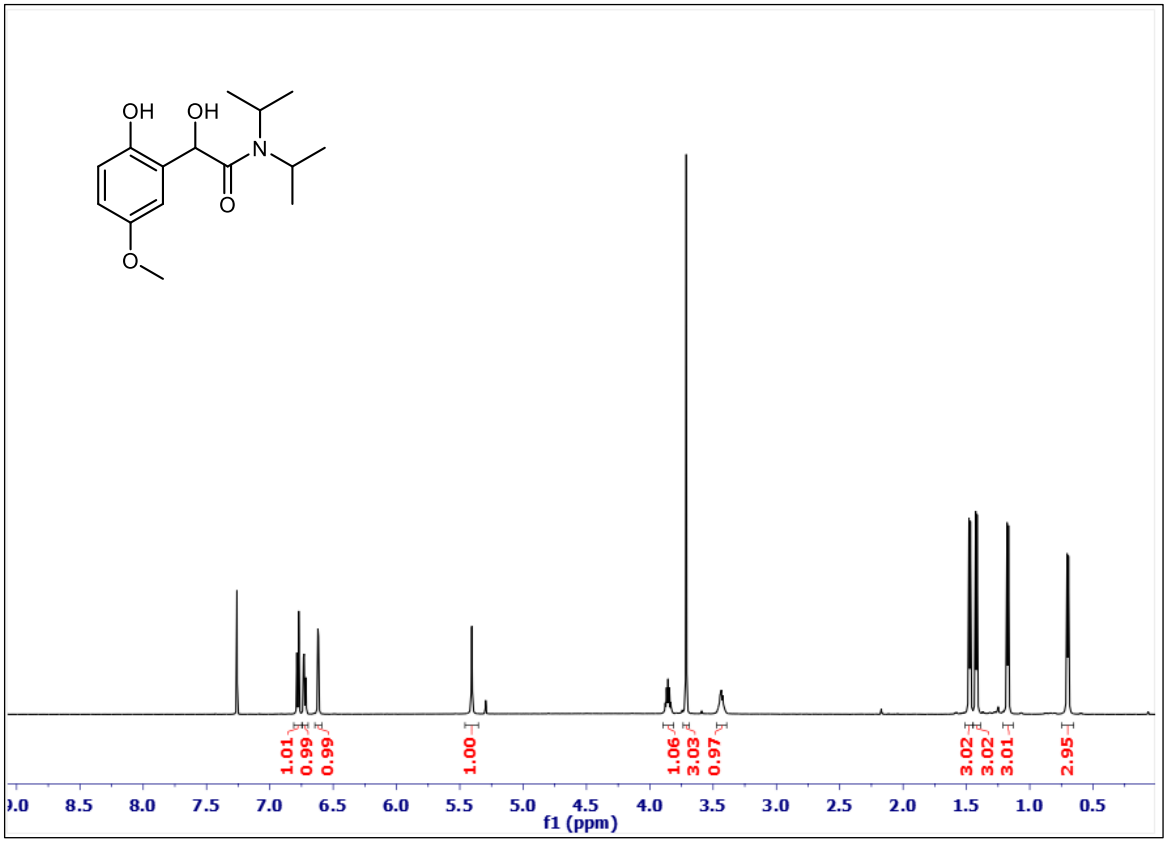


^{19}F NMR (565 MHz, CD_3OD)

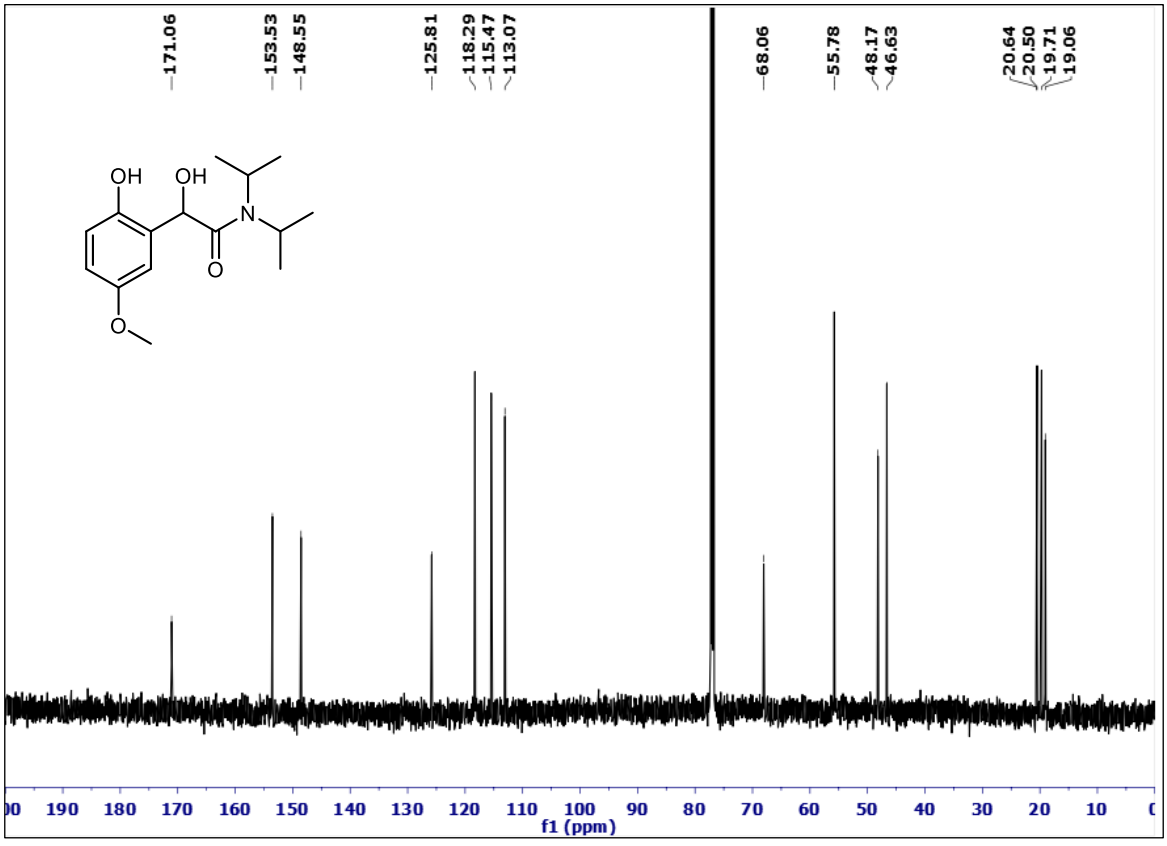


2-Hydroxy-2-(2-hydroxy-5-methoxyphenyl)-*N*,*N*-diisopropylacetamide (3f)

^{1}H NMR (600 MHz, $CDCl_3$)

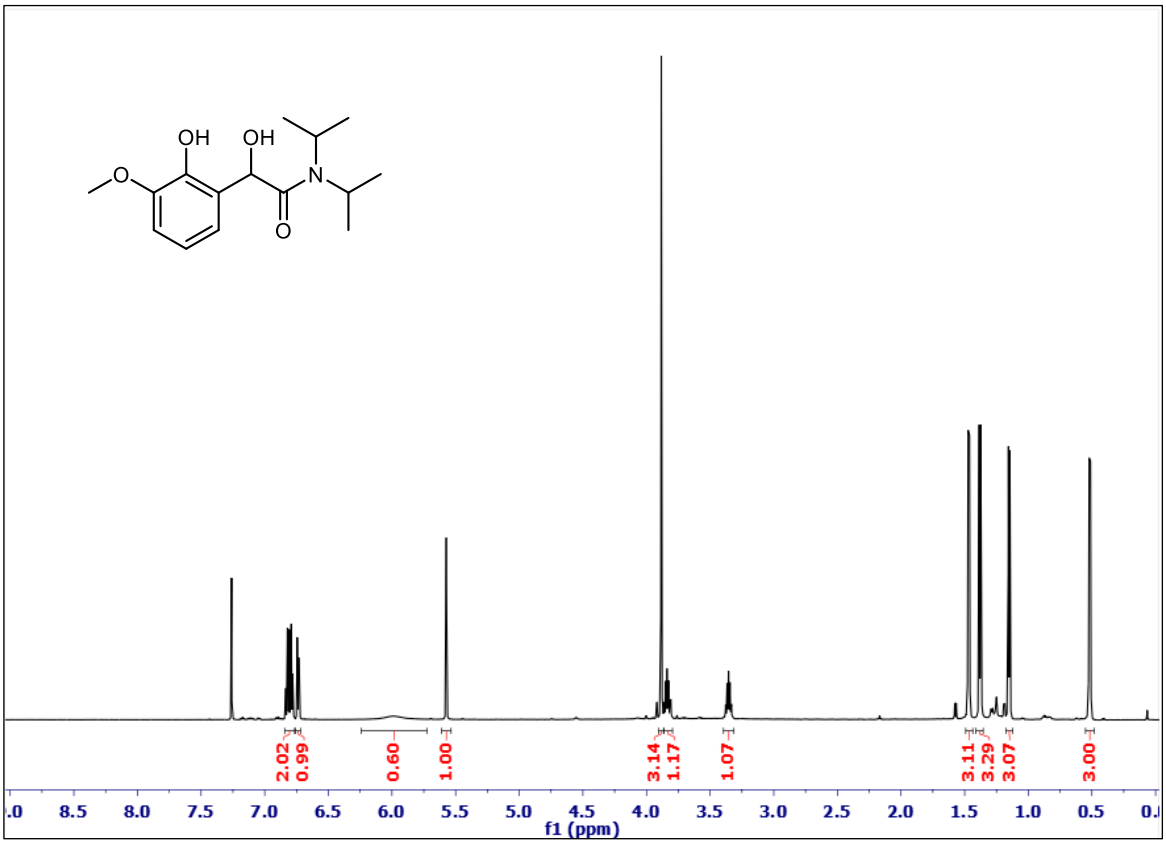


^{13}C NMR (150 MHz, $CDCl_3$)

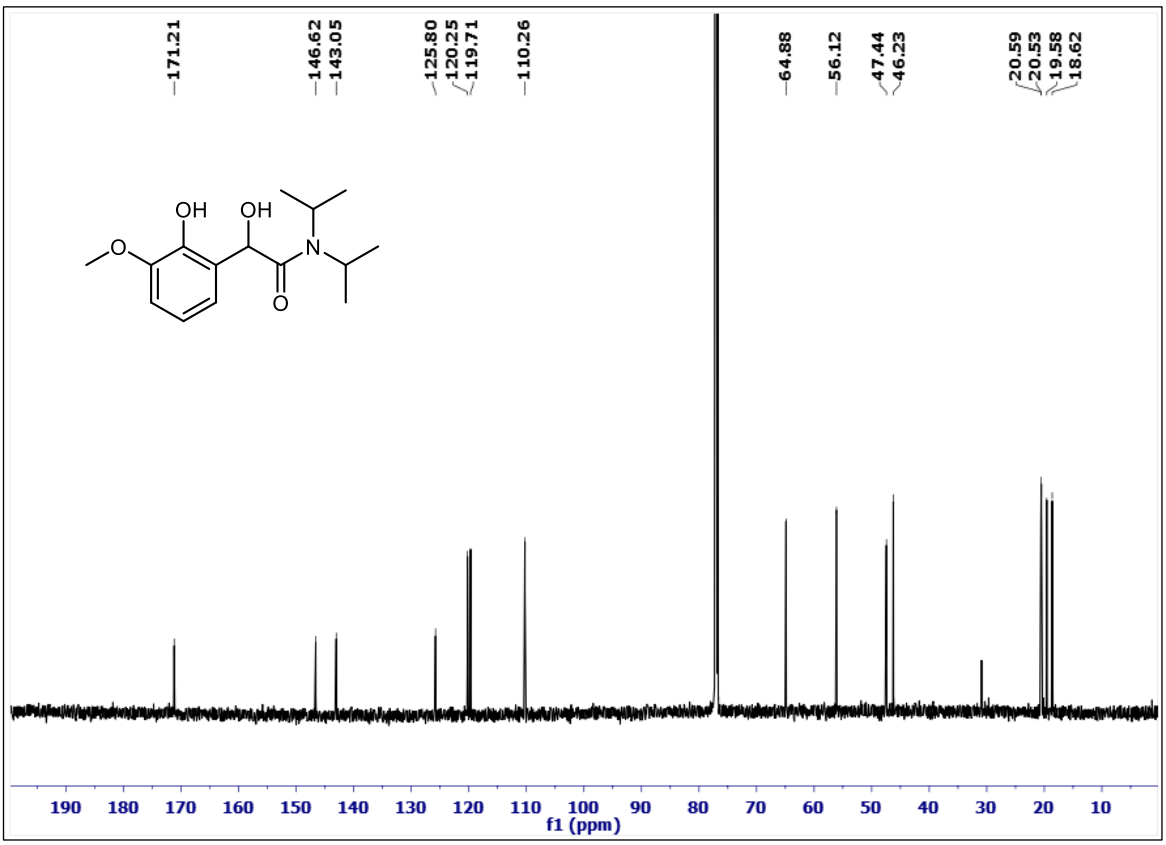


2-Hydroxy-2-(2-hydroxy-3-methoxyphenyl)-*N*,*N*-diisopropylacetamide (3g)

^{1}H NMR (600 MHz, $CDCl_3$)

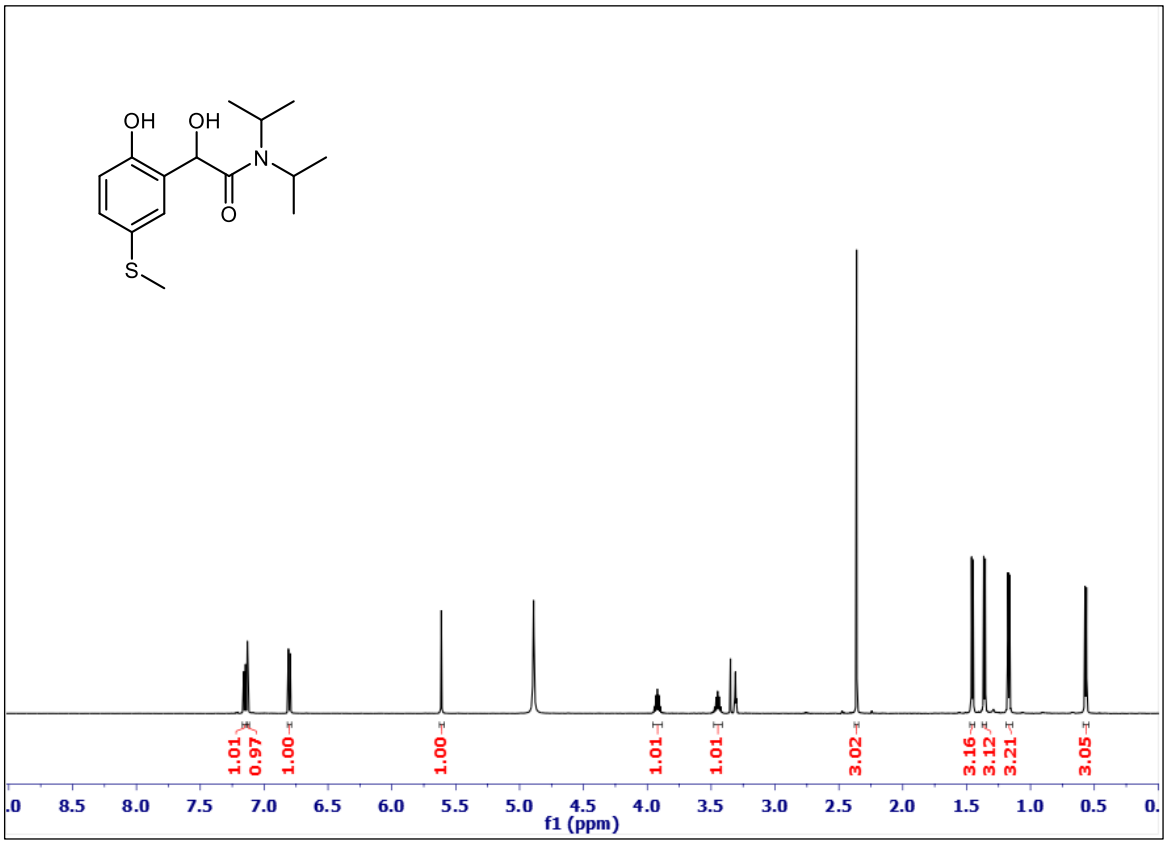


^{13}C NMR (150 MHz, $CDCl_3$)

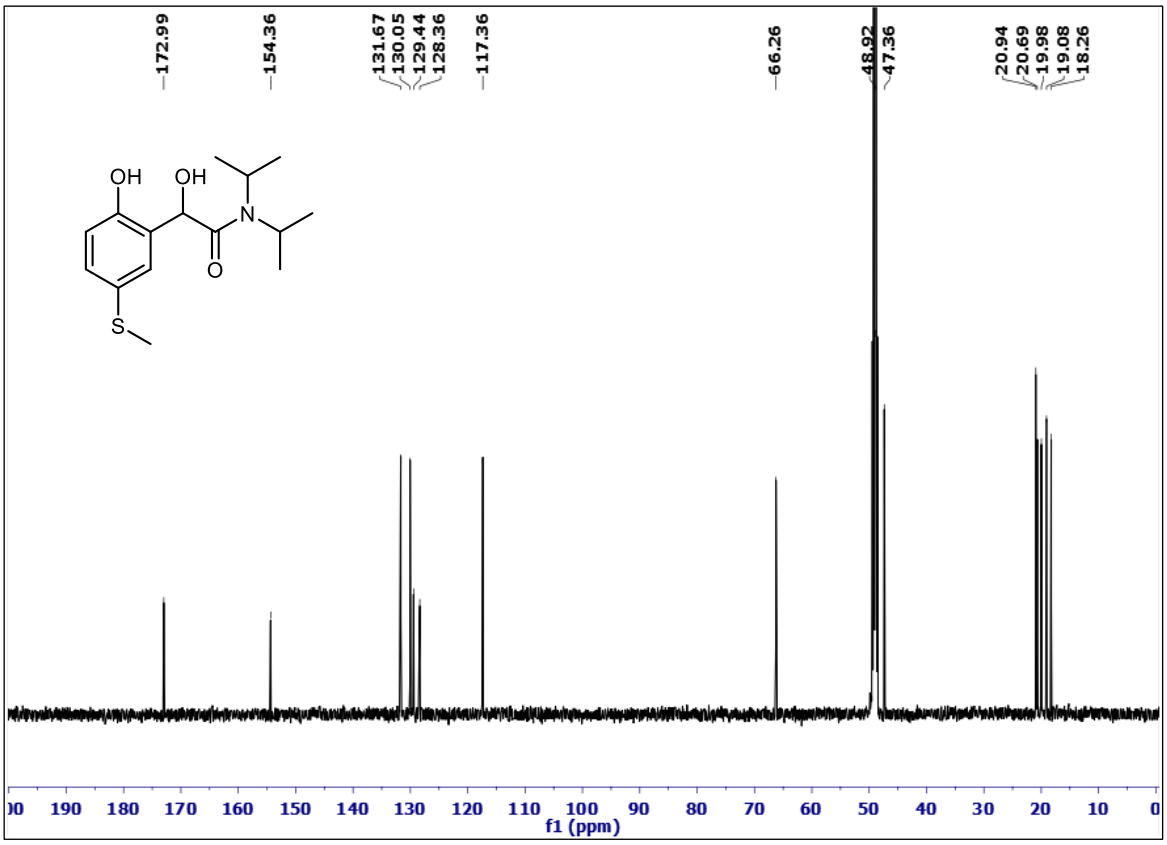


2-Hydroxy-2-(2-hydroxy-5-(methylthio)phenyl)-*N,N*-diisopropylacetamide (3h)

^{1}H NMR (600 MHz, CD_3OD)

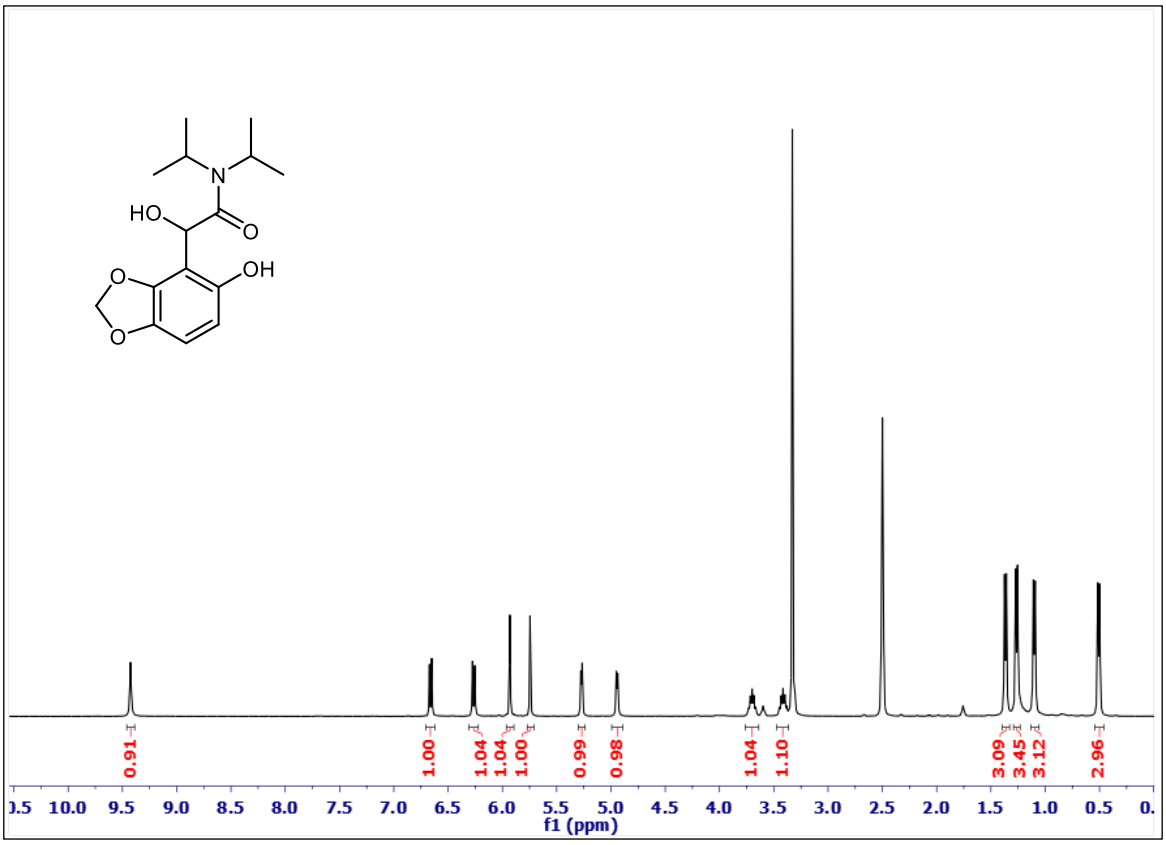


^{13}C NMR (150 MHz, CD_3OD)

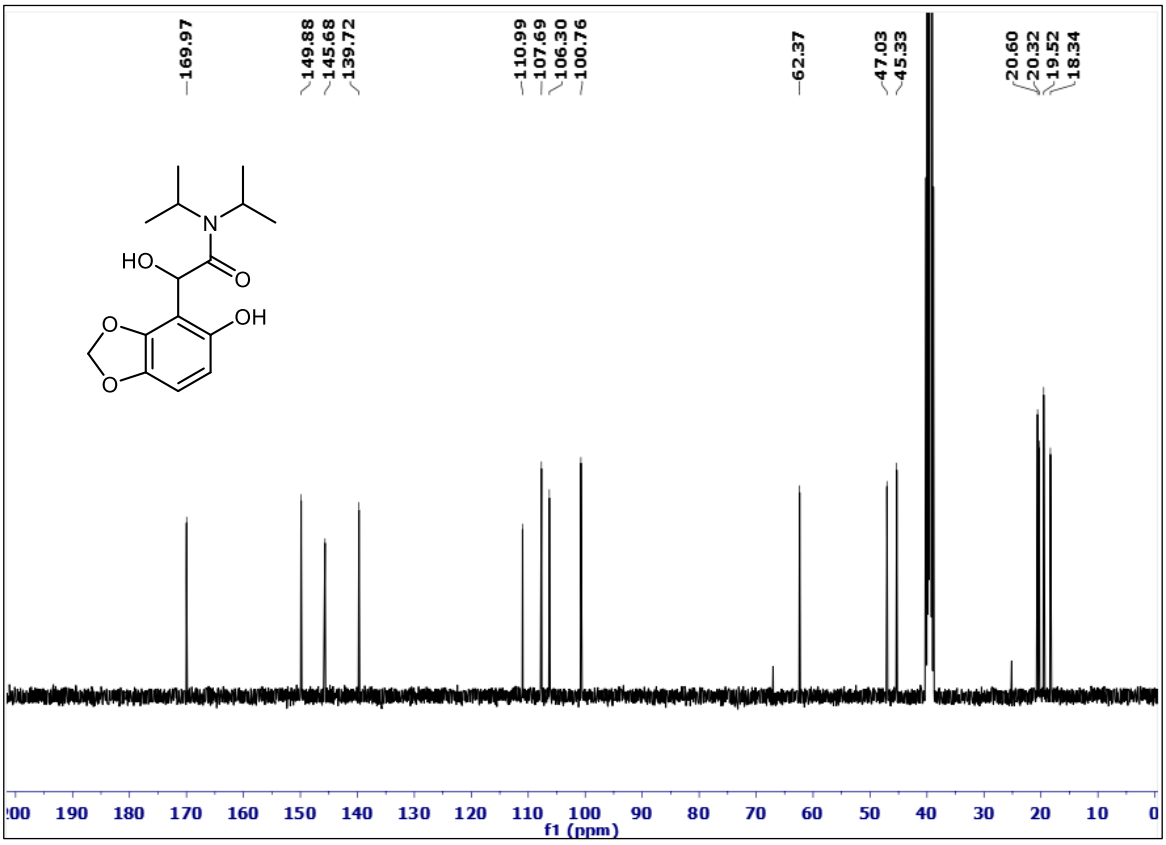


2-Hydroxy-2-(5-hydroxybenzo[d][1,3]dioxol-4-yl)-*N*,*N*-diisopropylacetamide (3i)

^{1}H NMR (400 MHz, DMSO-d_6)

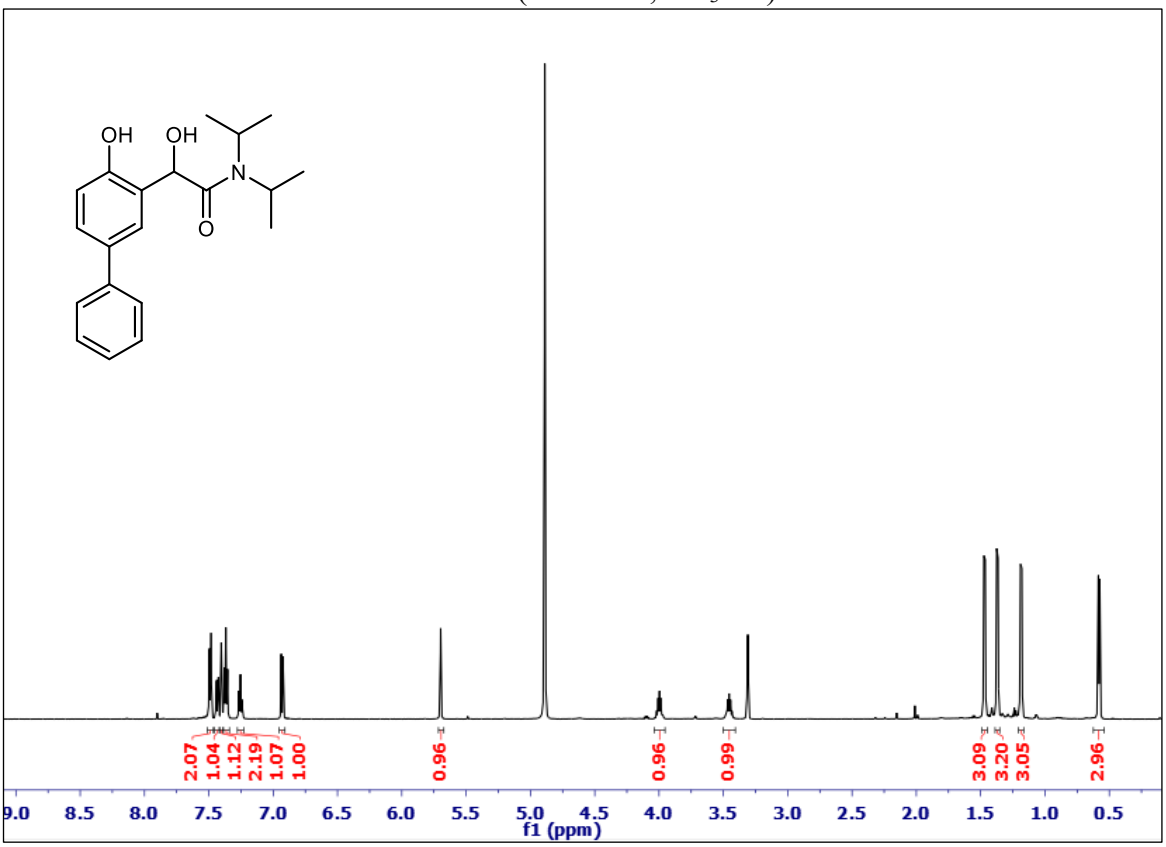


^{13}C NMR (100 MHz, DMSO-d_6)

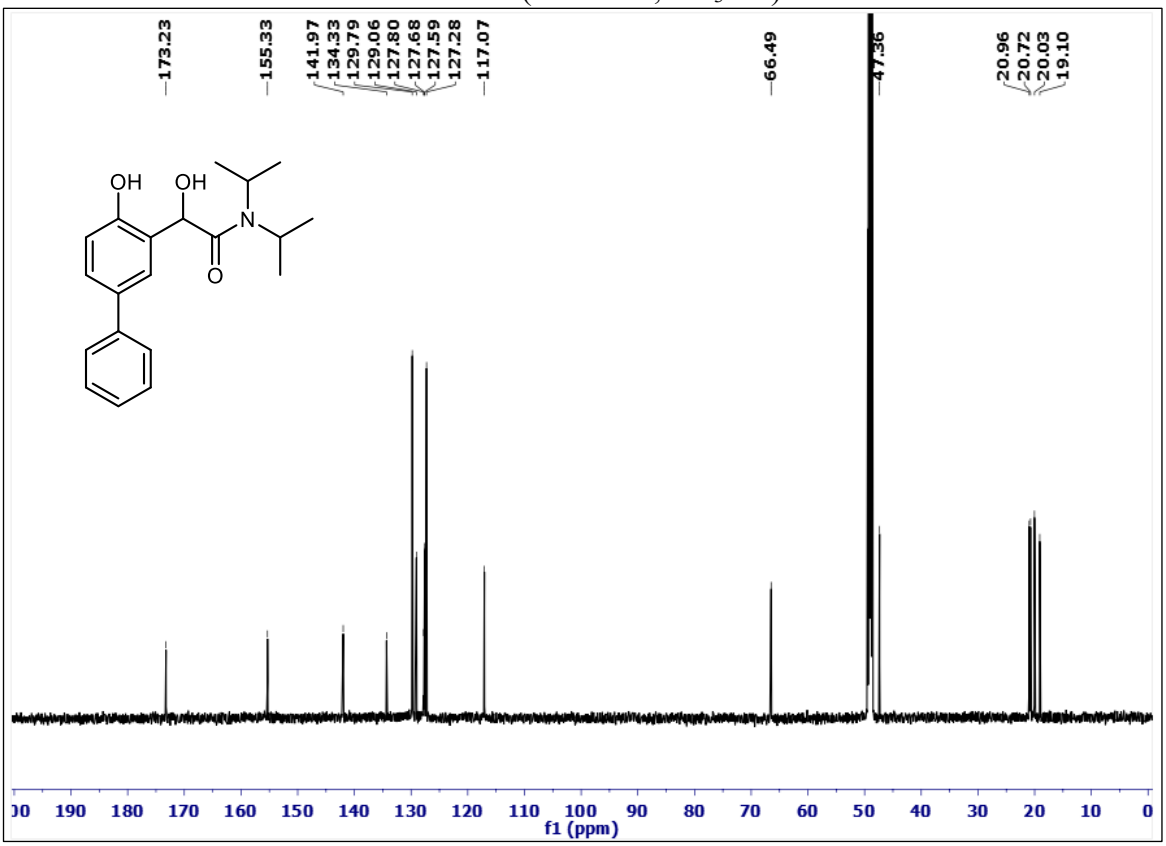


2-Hydroxy-2-(4-hydroxy-[1,1'-biphenyl]-3-yl)-*N*,*N*-diisopropylacetamide (3j)

^{1}H NMR (600 MHz, CD_3OD)

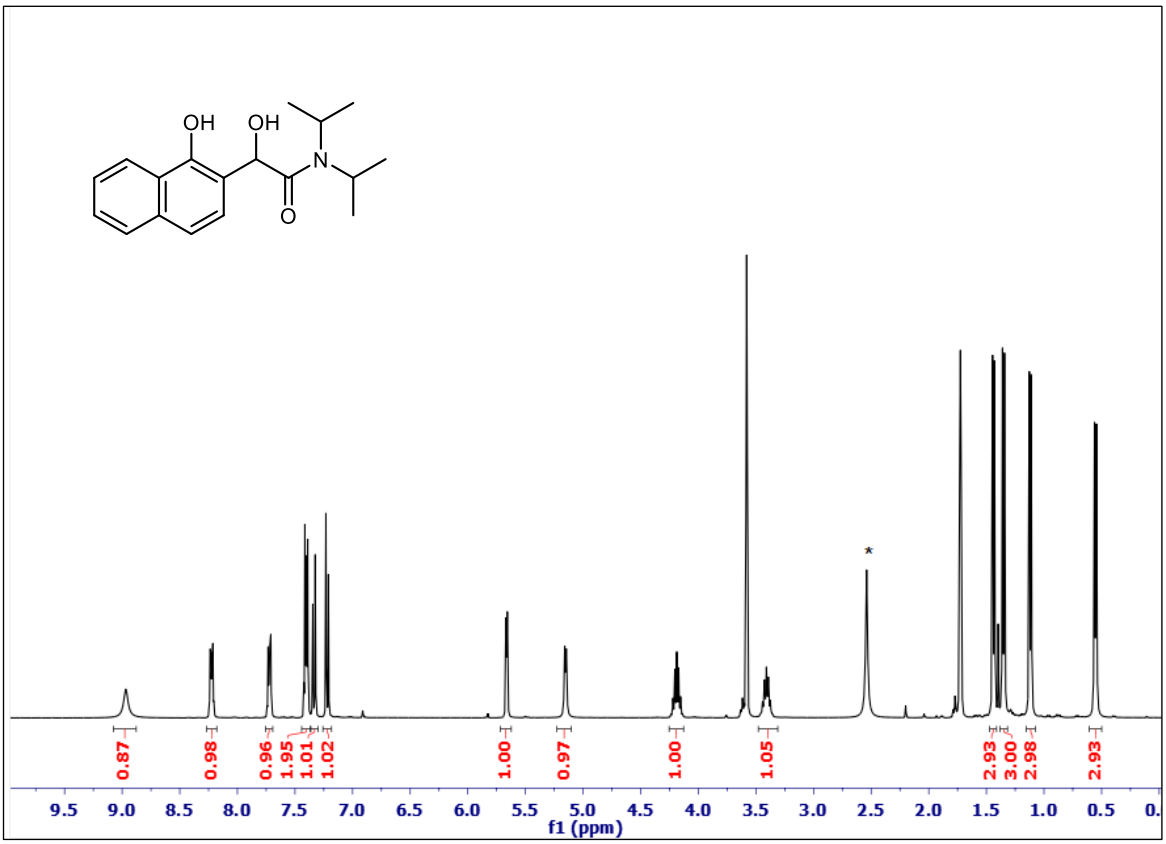


^{13}C NMR (150 MHz, CD_3OD)



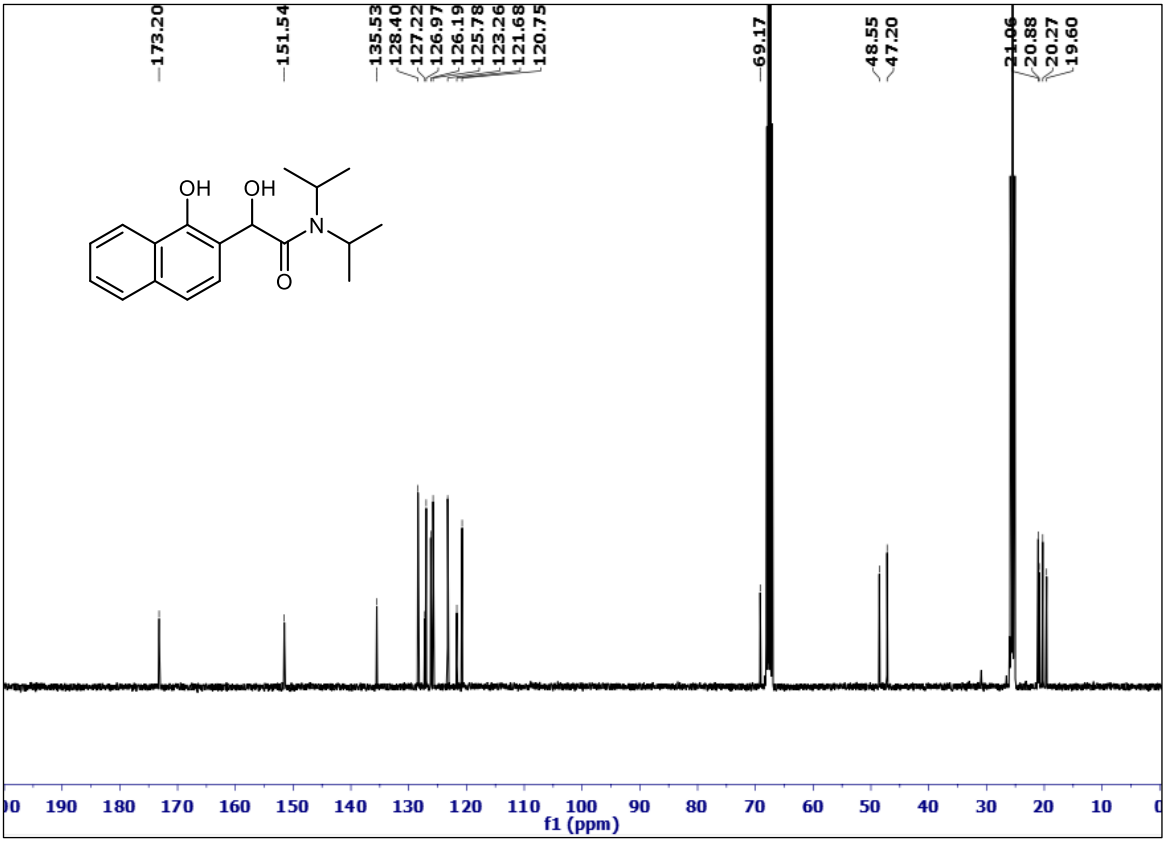
2-Hydroxy-2-(1-hydroxynaphthalen-2-yl)-*N*,*N*-diisopropylacetamide (3k)

^{1}H NMR (400 MHz, THF-d_8)



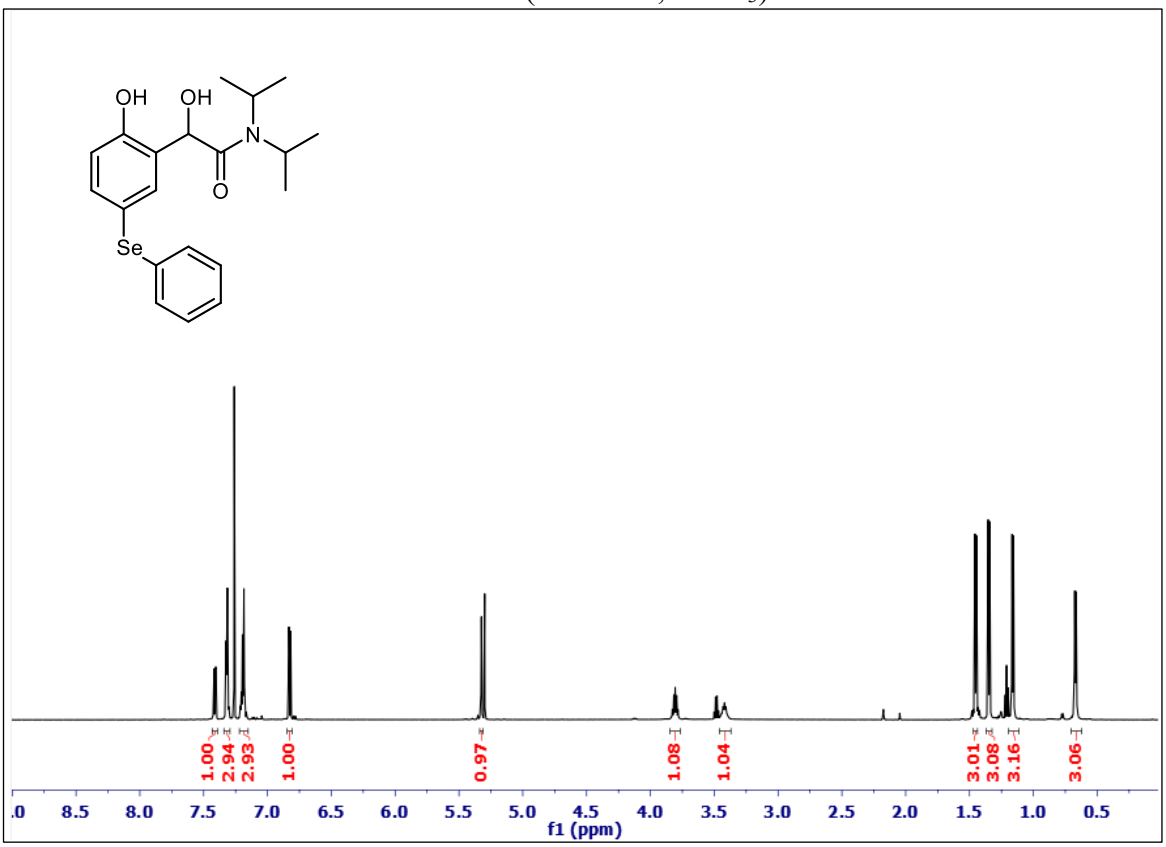
*H_2O residual peak

^{13}C NMR (100 MHz, THF-d_8)

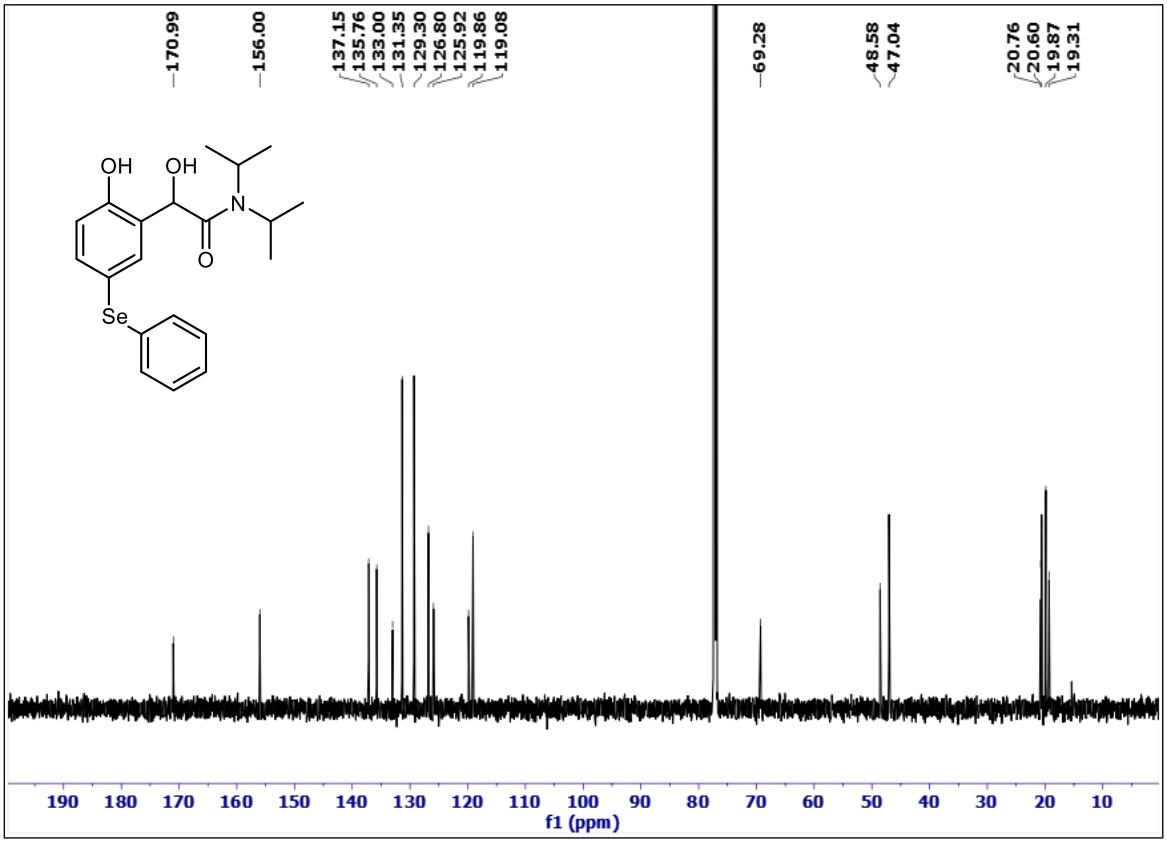


2-Hydroxy-2-(2-hydroxy-5-(phenylselanyl)phenyl)-*N*,*N*-diisopropylacetamide (3l)

^{1}H NMR (600 MHz, $CDCl_3$)

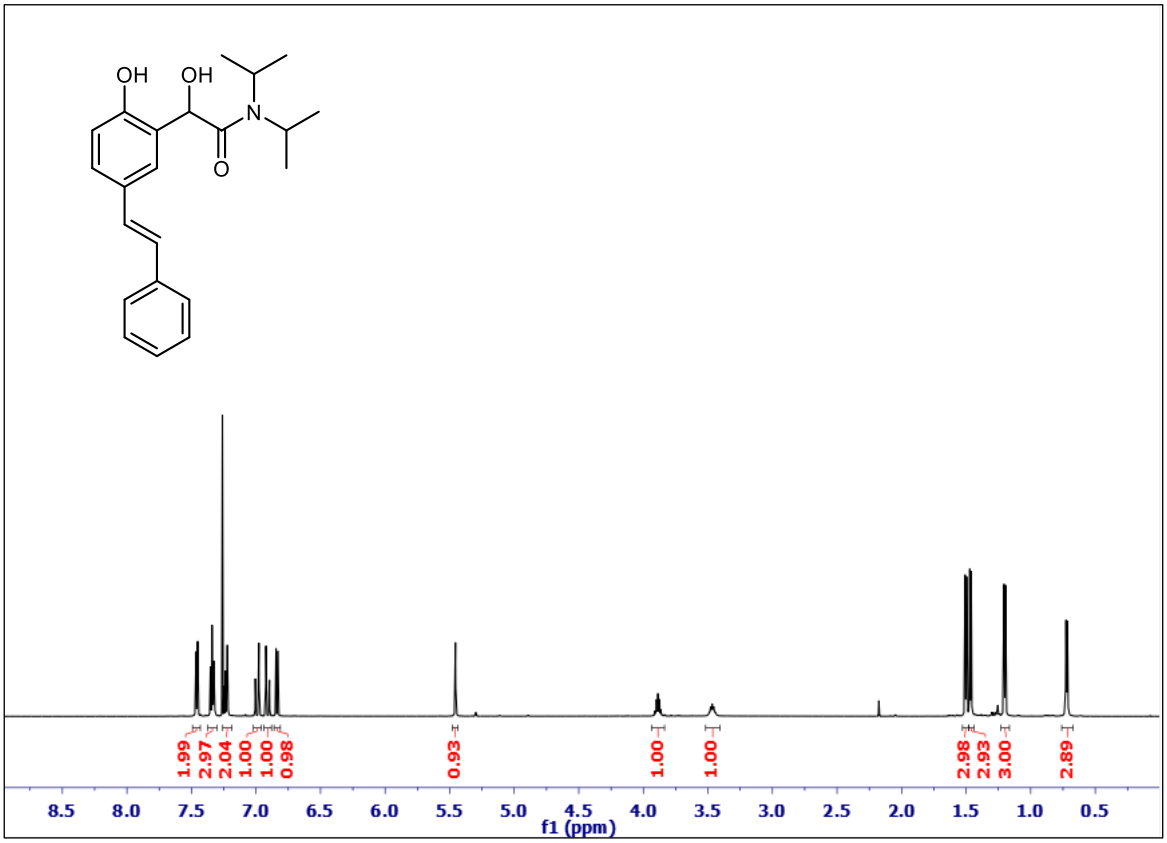


^{13}C NMR (150 MHz, $CDCl_3$)

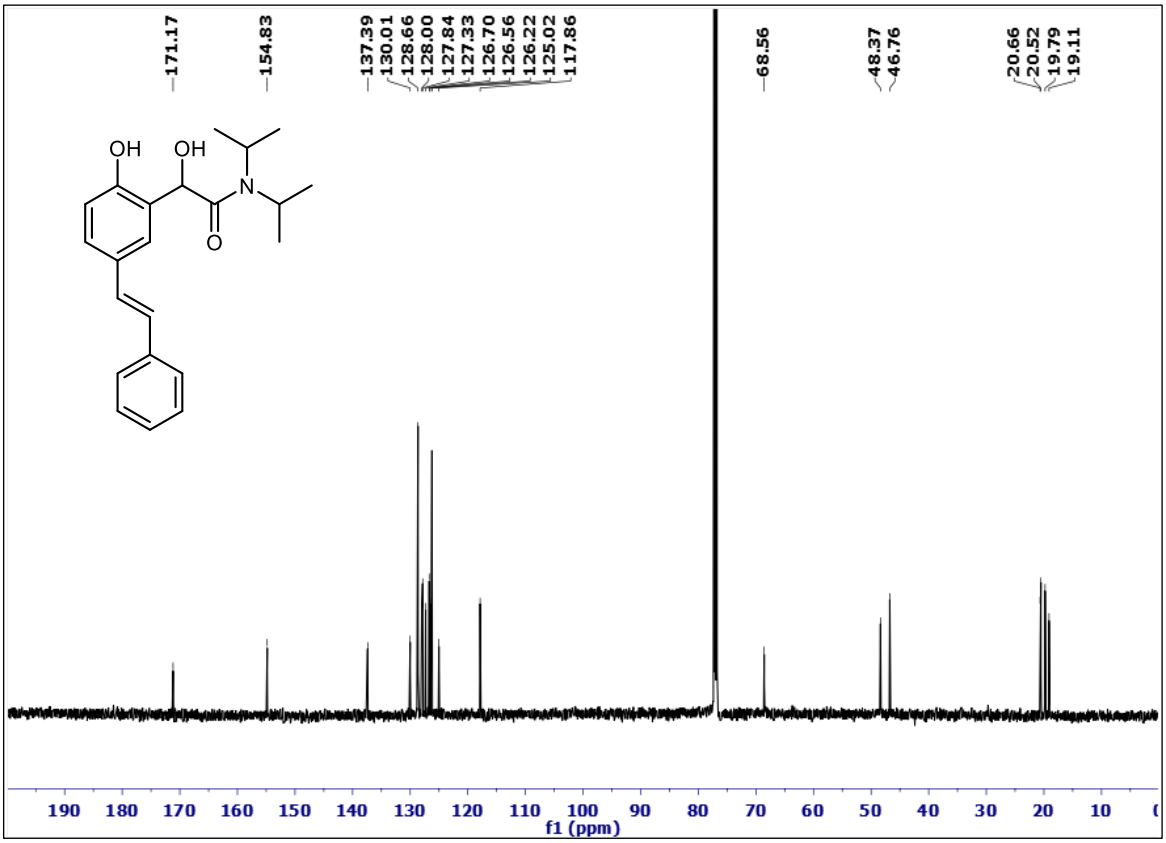


(*E*)-2-Hydroxy-2-(2-hydroxy-5-styrylphenyl)-*N*,*N*-diisopropylacetamide (3m)

^{1}H NMR (600 MHz, $CDCl_3$)

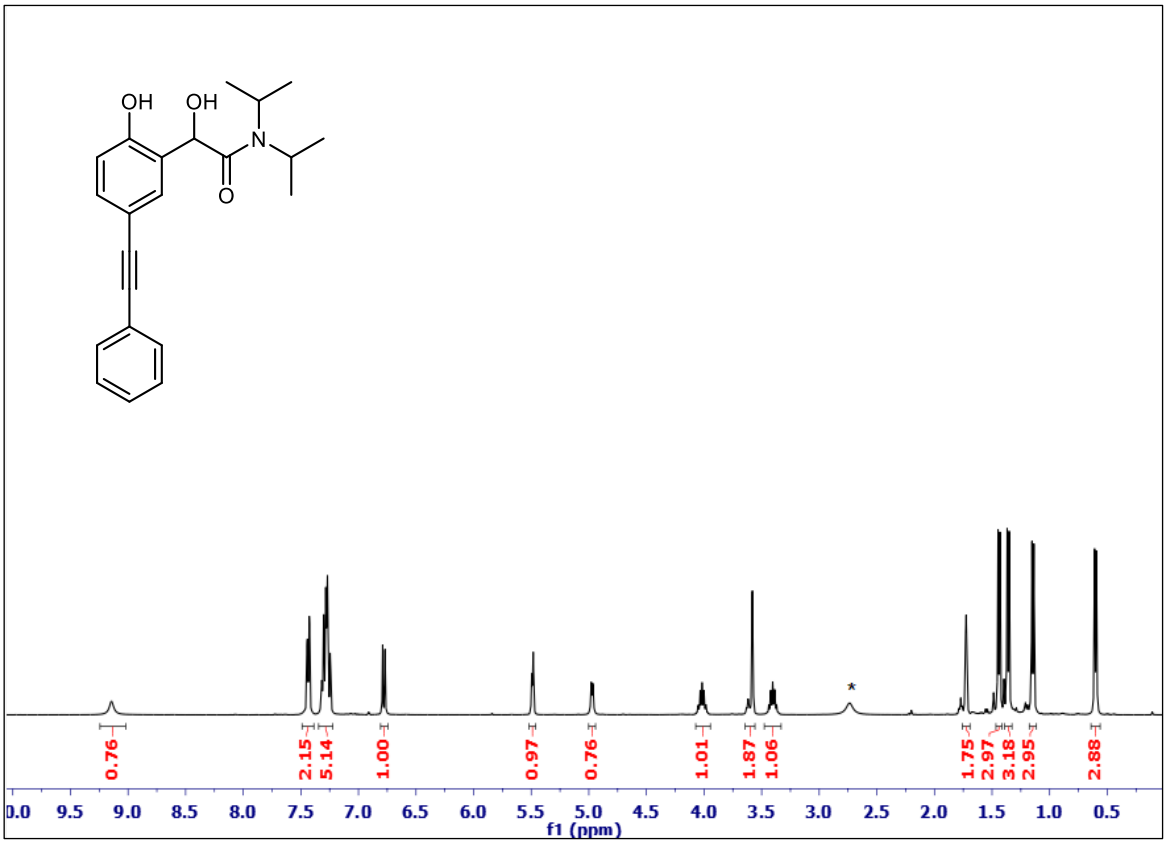


^{13}C NMR (150 MHz, $CDCl_3$)



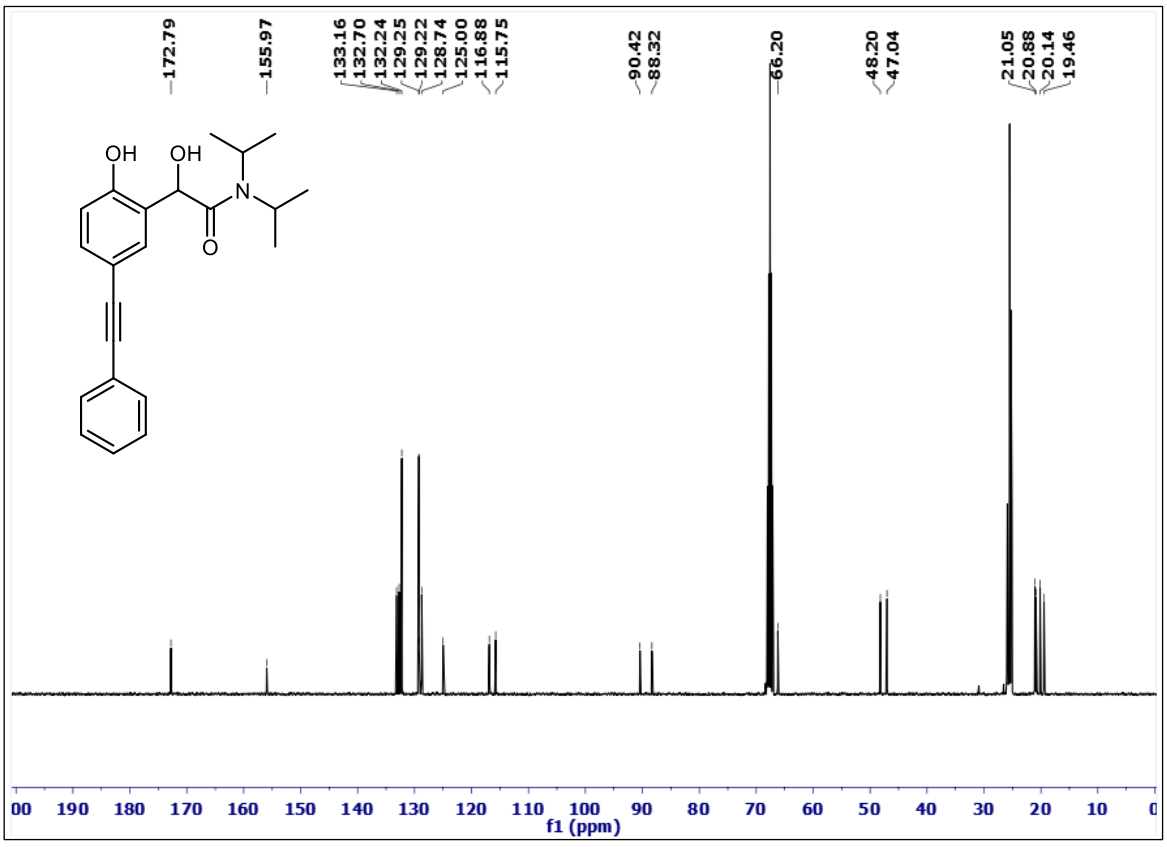
2-Hydroxy-2-(2-hydroxy-5-(phenylethynyl)phenyl)-*N*,*N*-diisopropylacetamide (3n)

^{1}H NMR (400 MHz, THF-d_8)



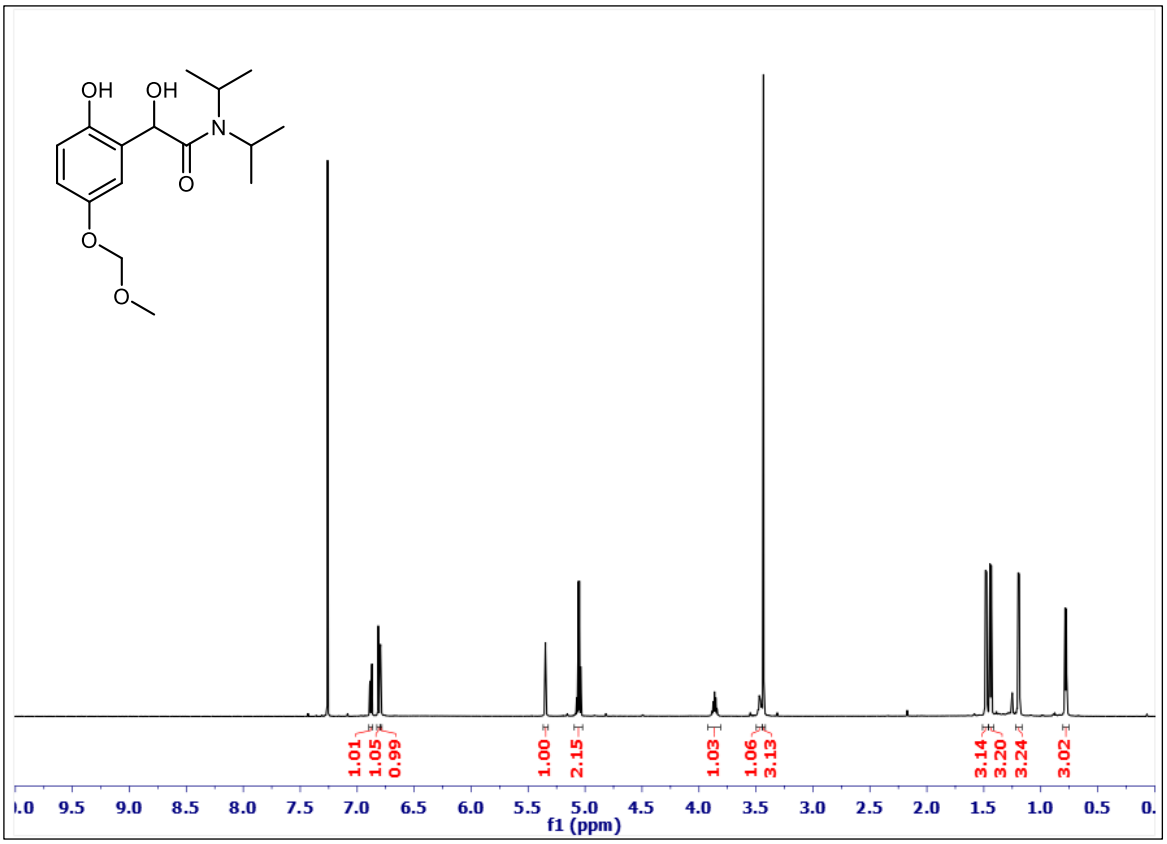
*H_2O residual peak

^{13}C NMR (100 MHz, THF-d_8)

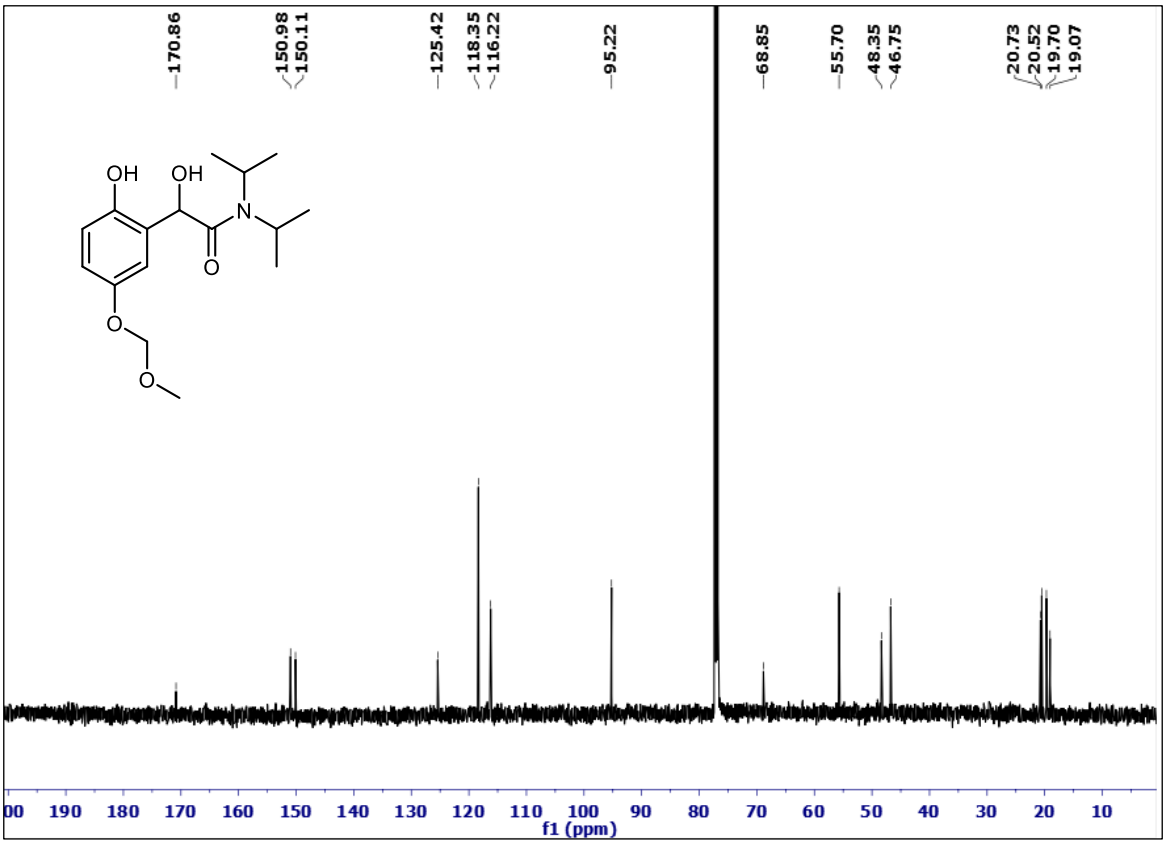


2-Hydroxy-2-(2-hydroxy-5-(methoxymethoxy)phenyl)-*N*,*N*-diisopropylacetamide (3o)

^{1}H NMR (600 MHz, $CDCl_3$)

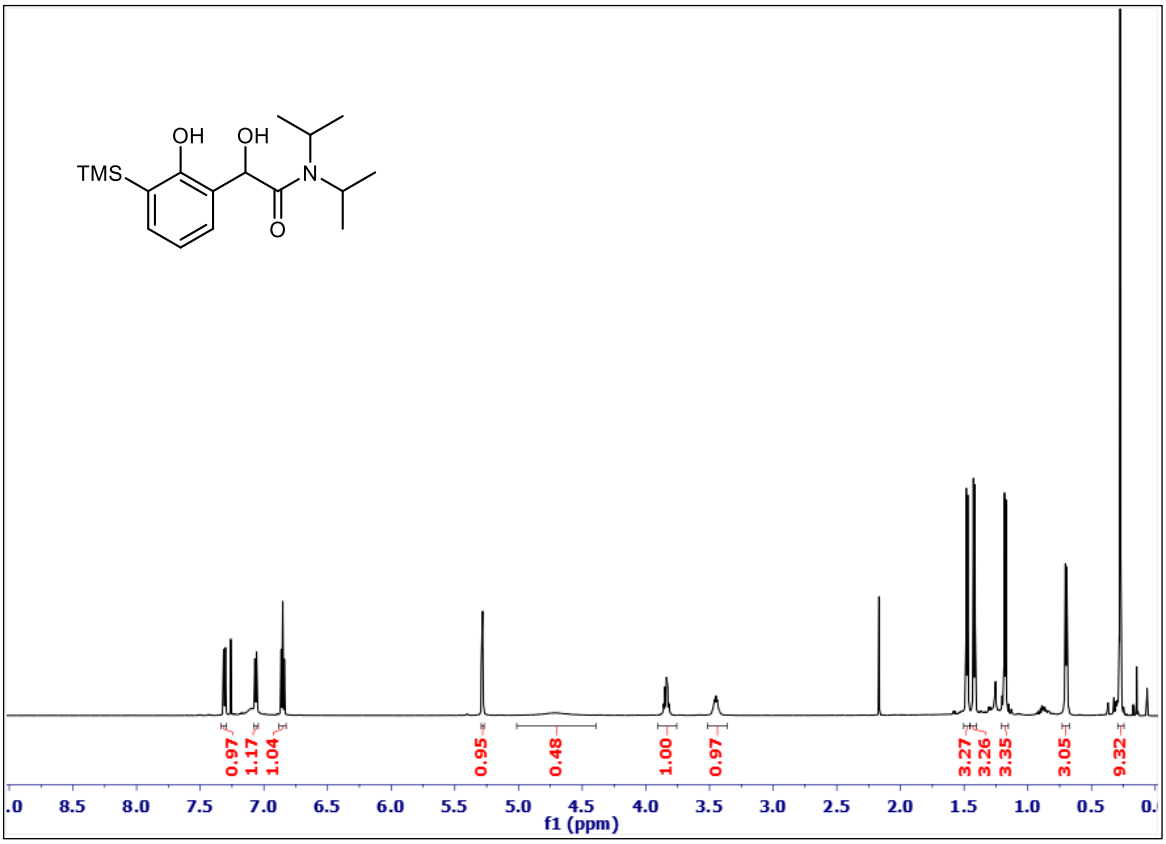


^{13}C NMR (150 MHz, $CDCl_3$)

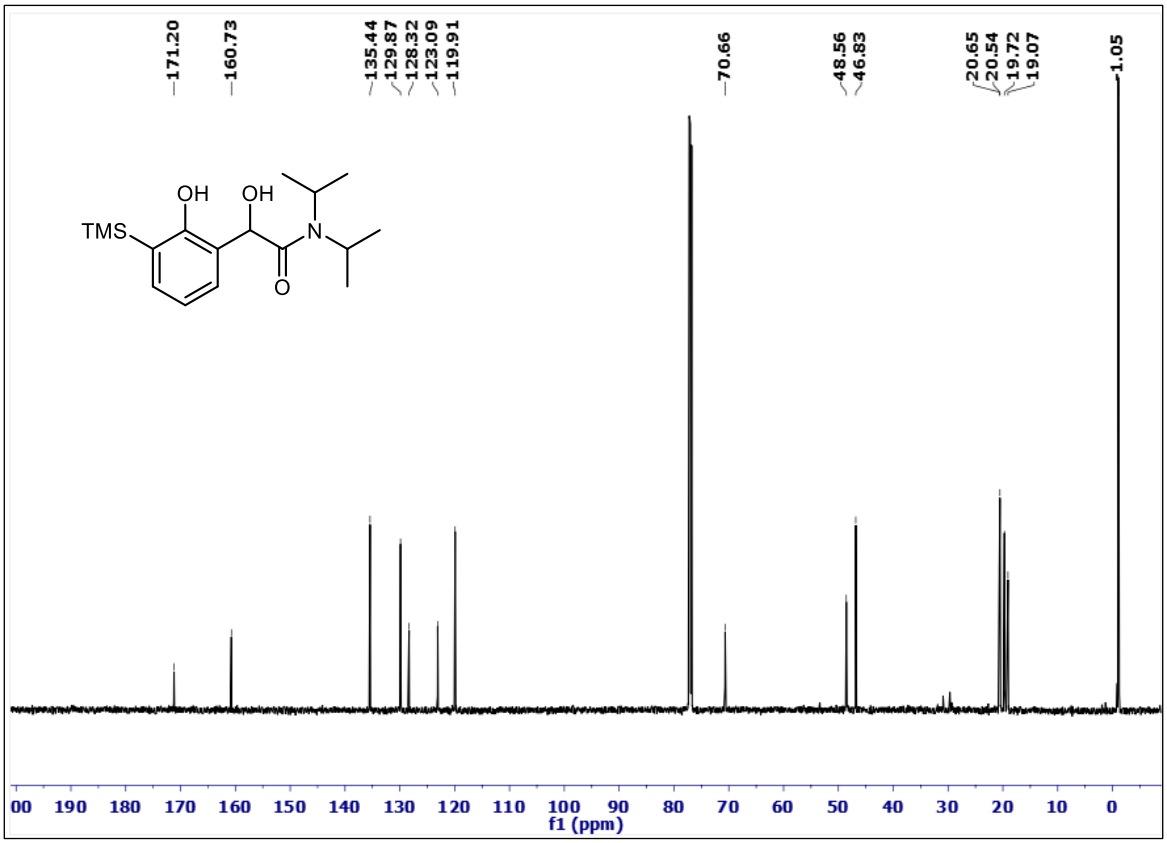


2-Hydroxy-2-(2-hydroxy-3-(trimethylsilyl)phenyl)-*N*,*N*-diisopropylacetamide (3p)

^{1}H NMR (600 MHz, $CDCl_3$)

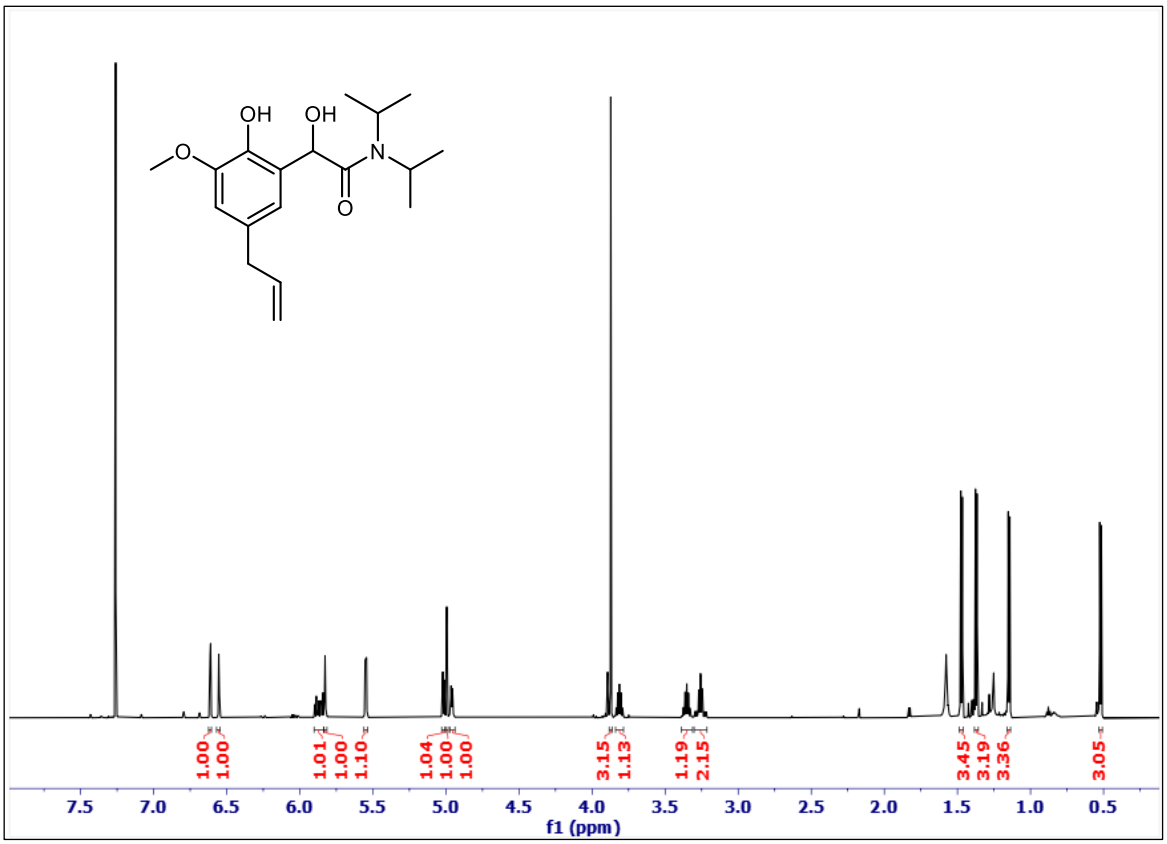


^{13}C NMR (150 MHz, $CDCl_3$)

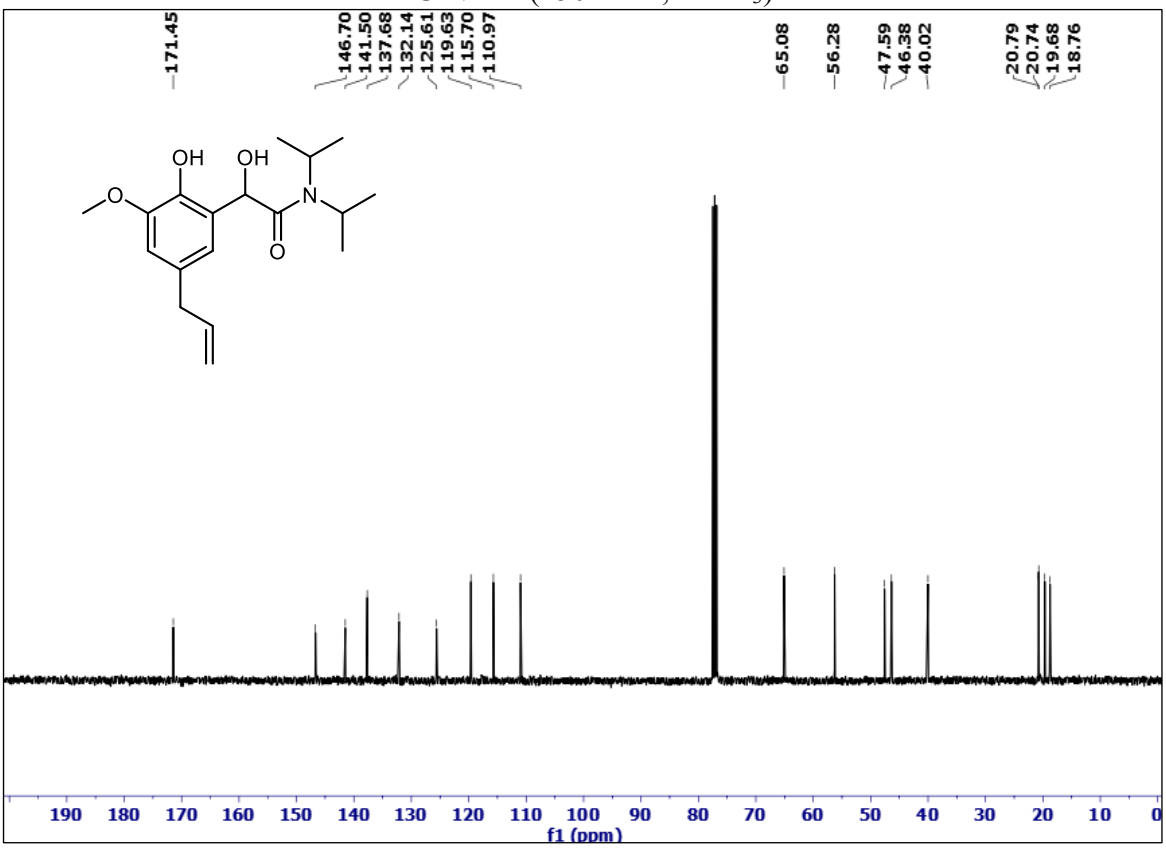


2-(5-Allyl-2-hydroxy-3-methoxyphenyl)-2-hydroxy-*N*,*N*-diisopropylacetamide (3q)

^{1}H NMR (600 MHz, $CDCl_3$)

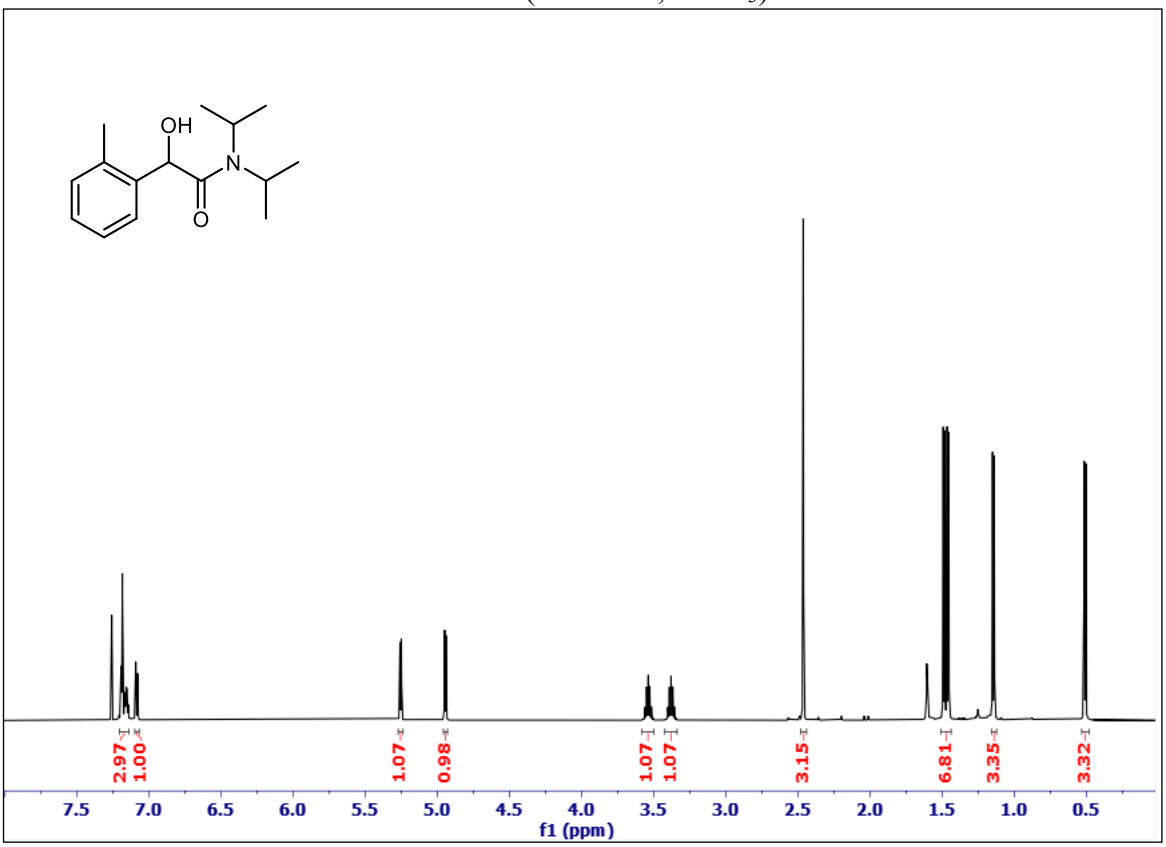


^{13}C NMR (150 MHz, $CDCl_3$)

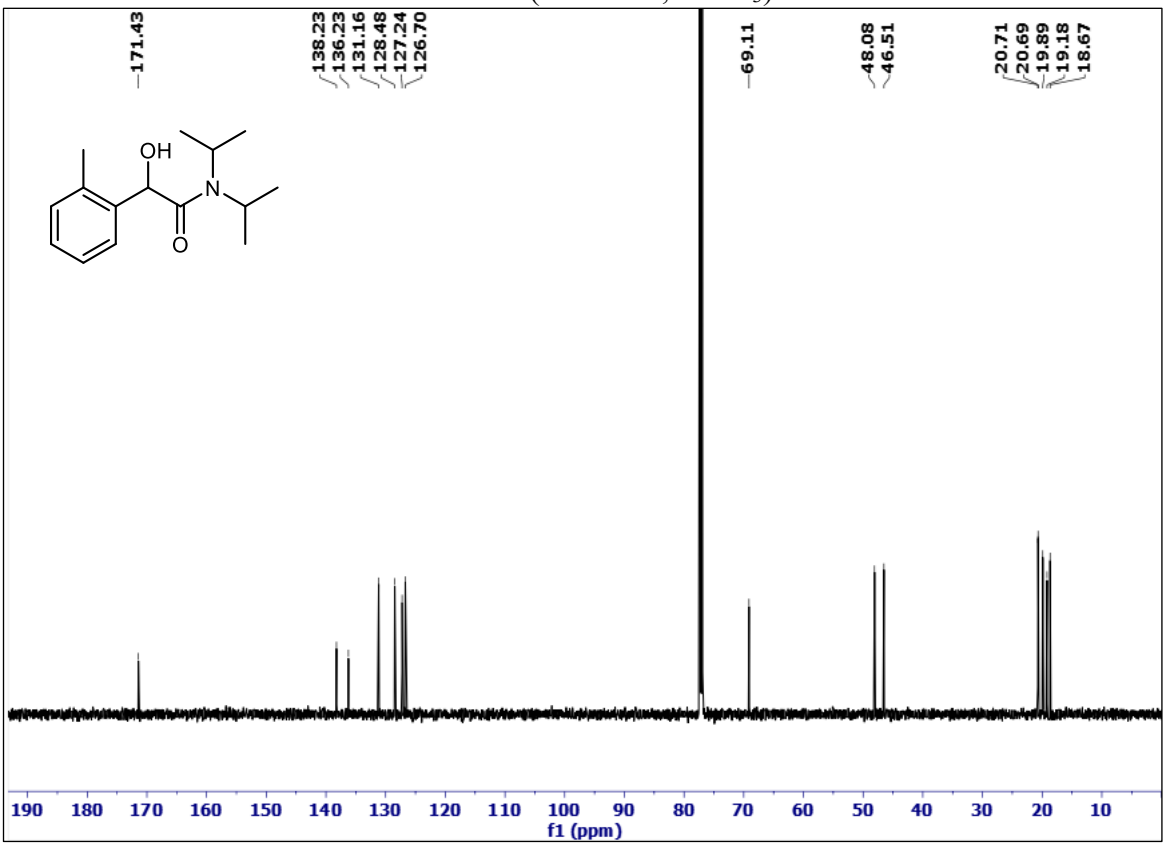


2-Hydroxy-*N*,*N*-diisopropyl-2-(*o*-tolyl)acetamide (3r)

^{1}H NMR (600 MHz, $CDCl_3$)

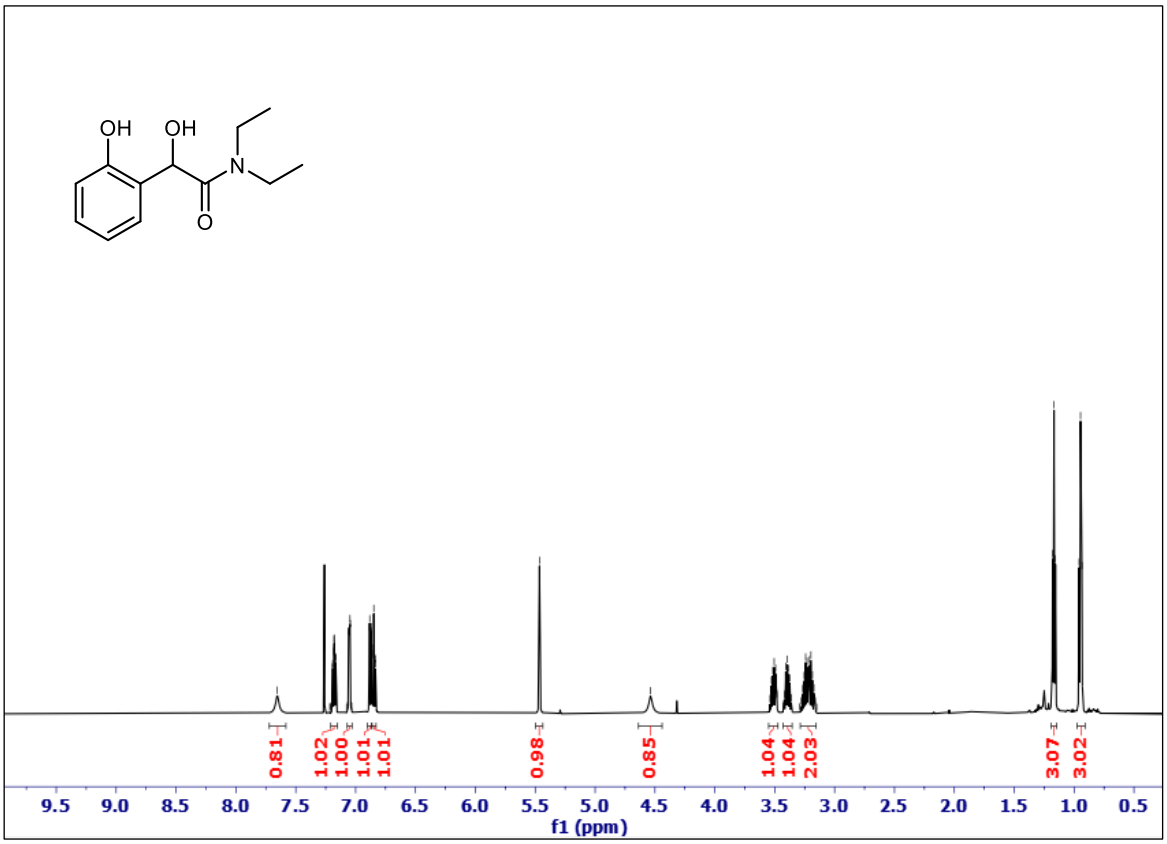


^{13}C NMR (150 MHz, $CDCl_3$)

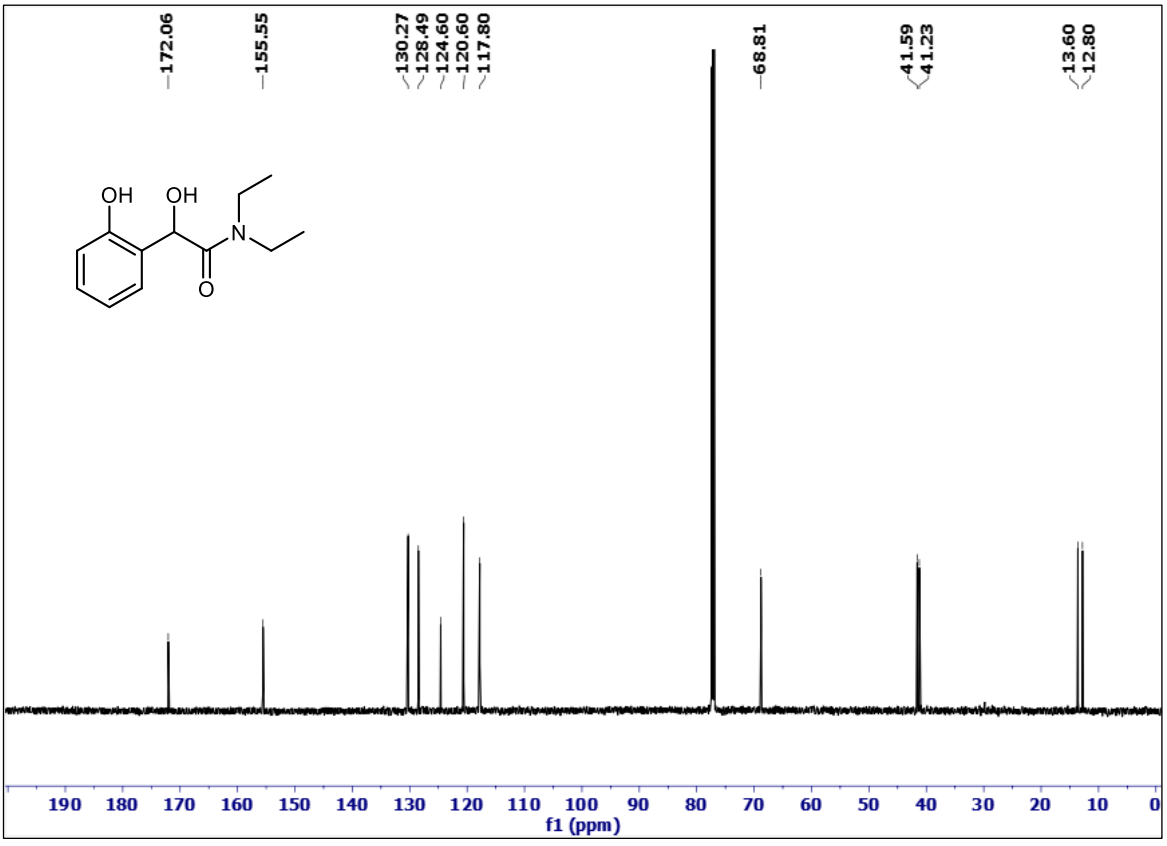


2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-diethyl acetamide (3s)

^{1}H NMR (600 MHz, $CDCl_3$)

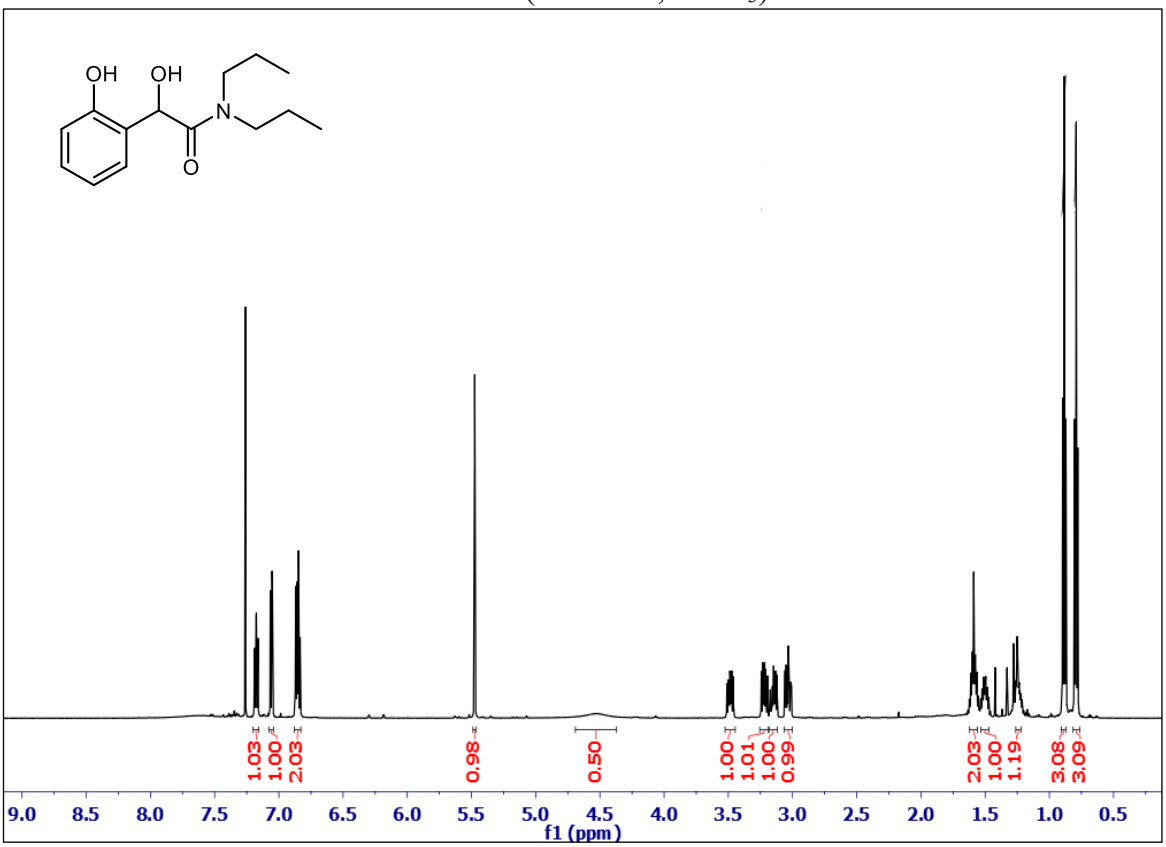


^{13}C NMR (150 MHz, $CDCl_3$)

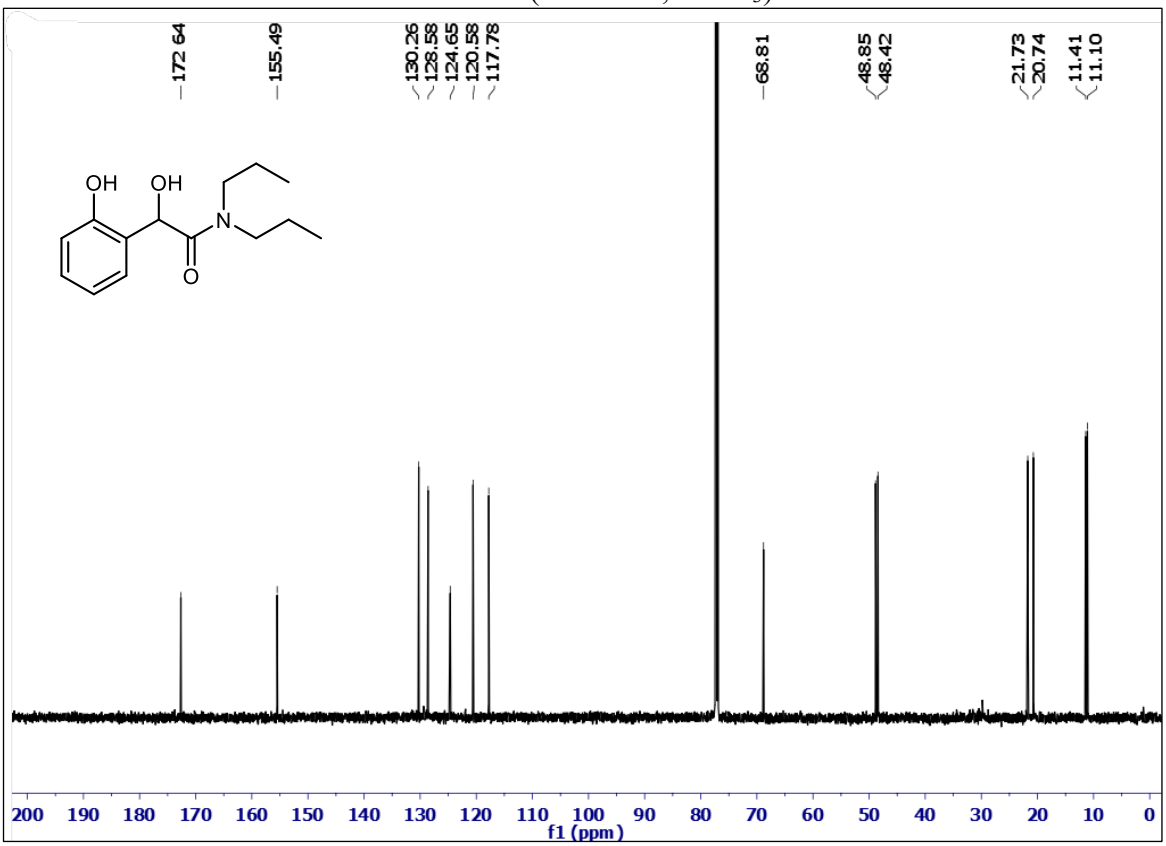


2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-dipropylacetamide (3t)

^{1}H NMR (600 MHz, $CDCl_3$)

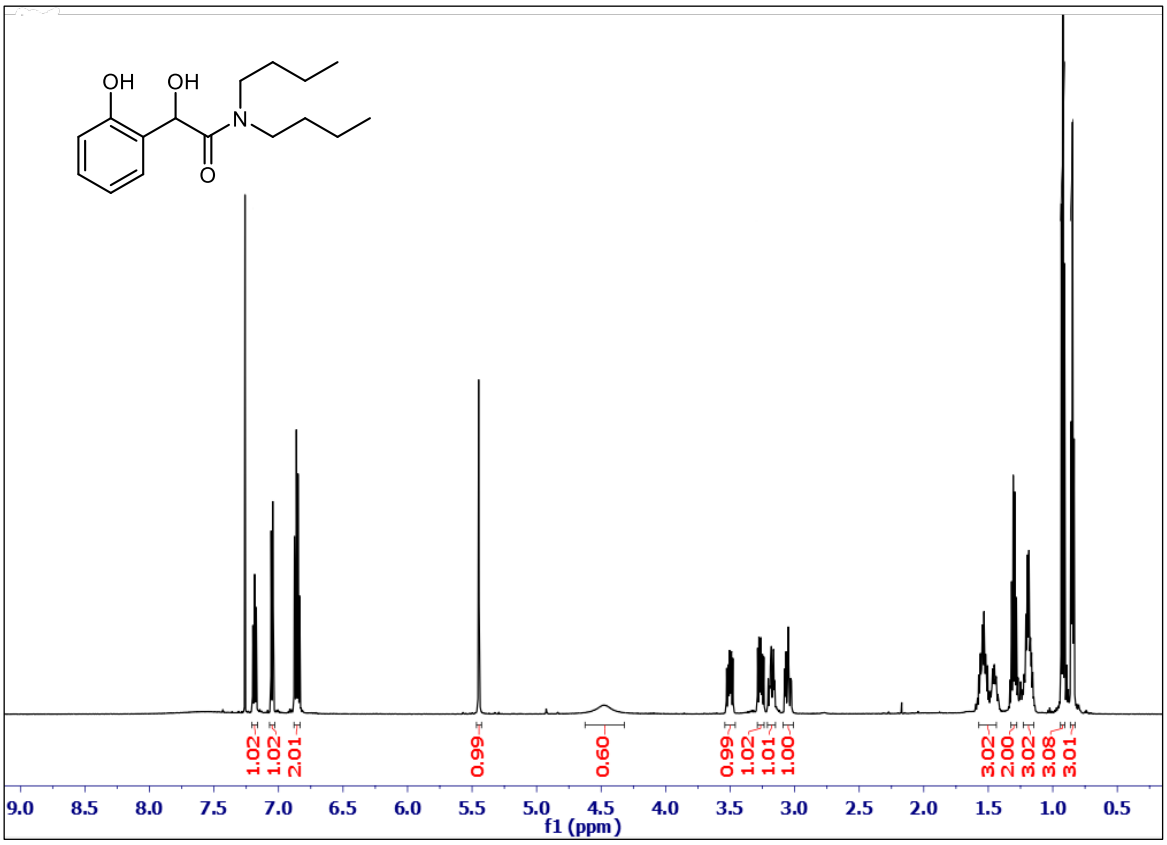


^{13}C NMR (150 MHz, $CDCl_3$)

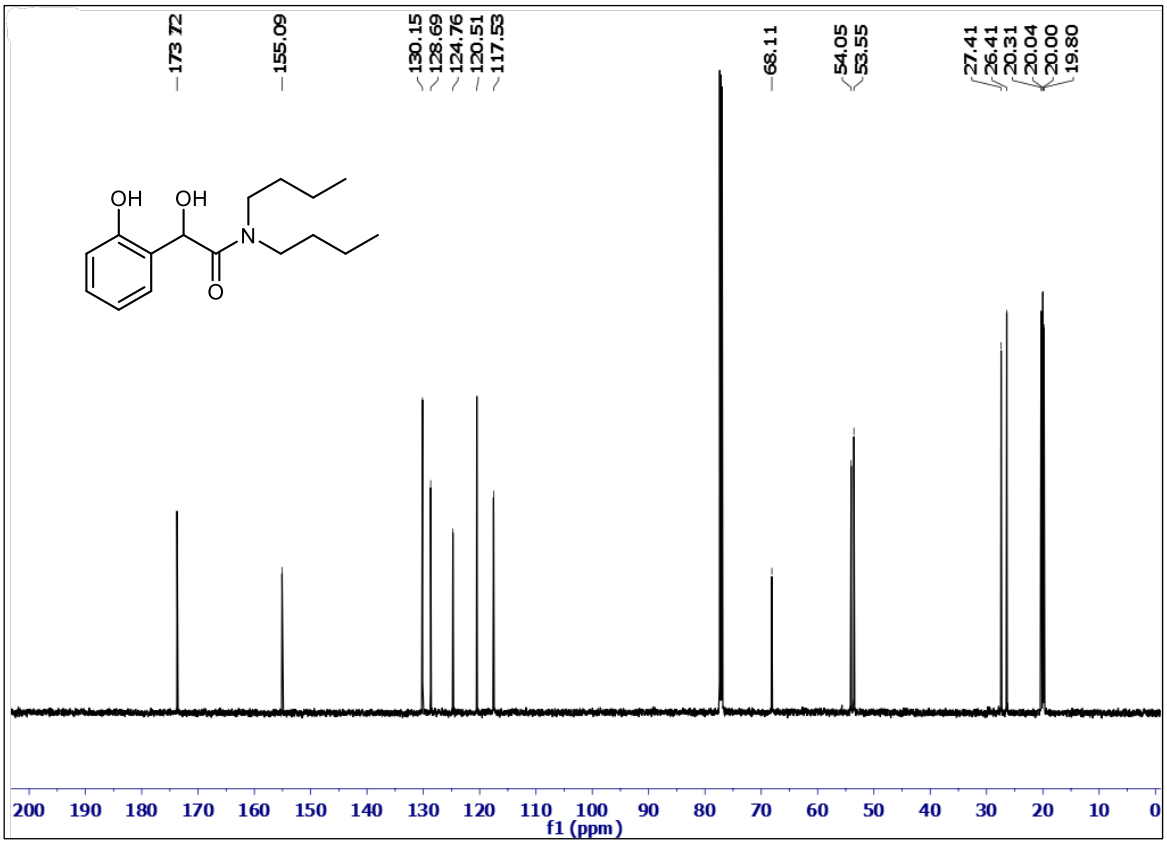


2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-dibutylacetamide (3u)

^{1}H NMR (600 MHz, $CDCl_3$)

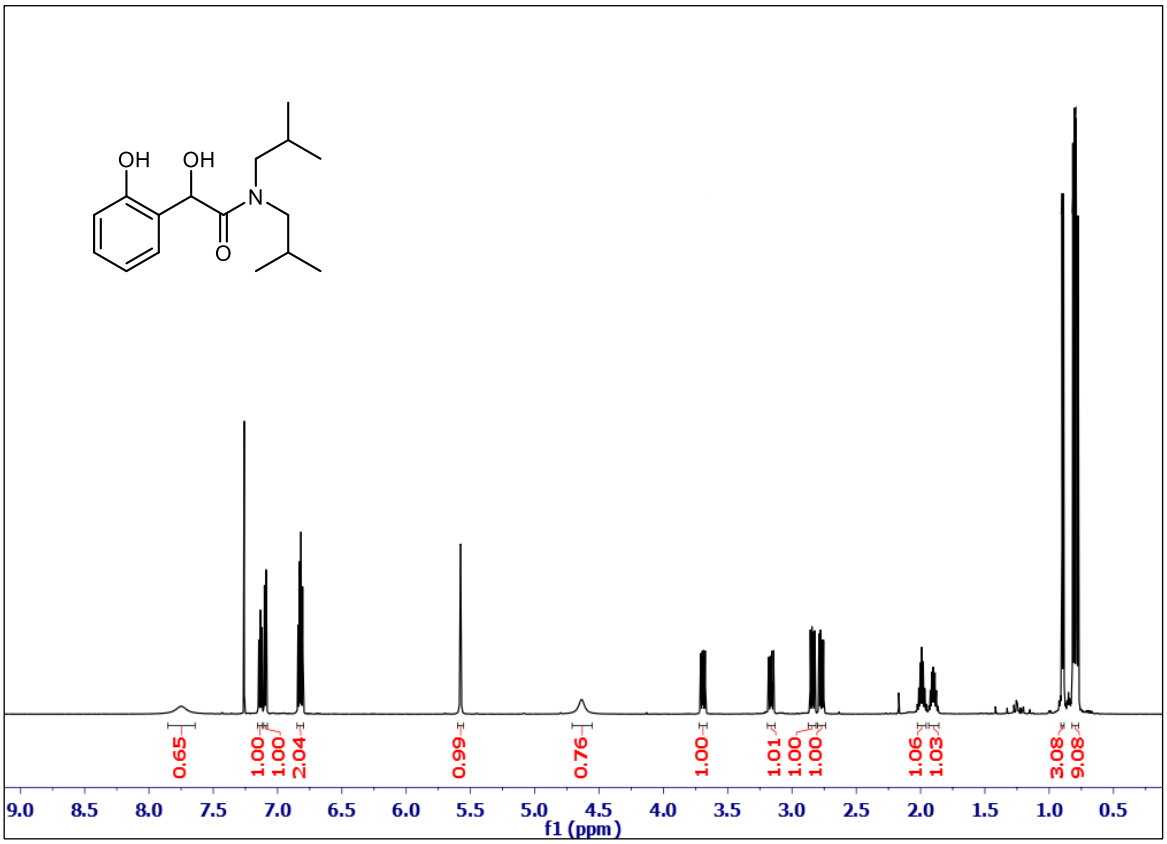


^{13}C NMR (150 MHz, $CDCl_3$)

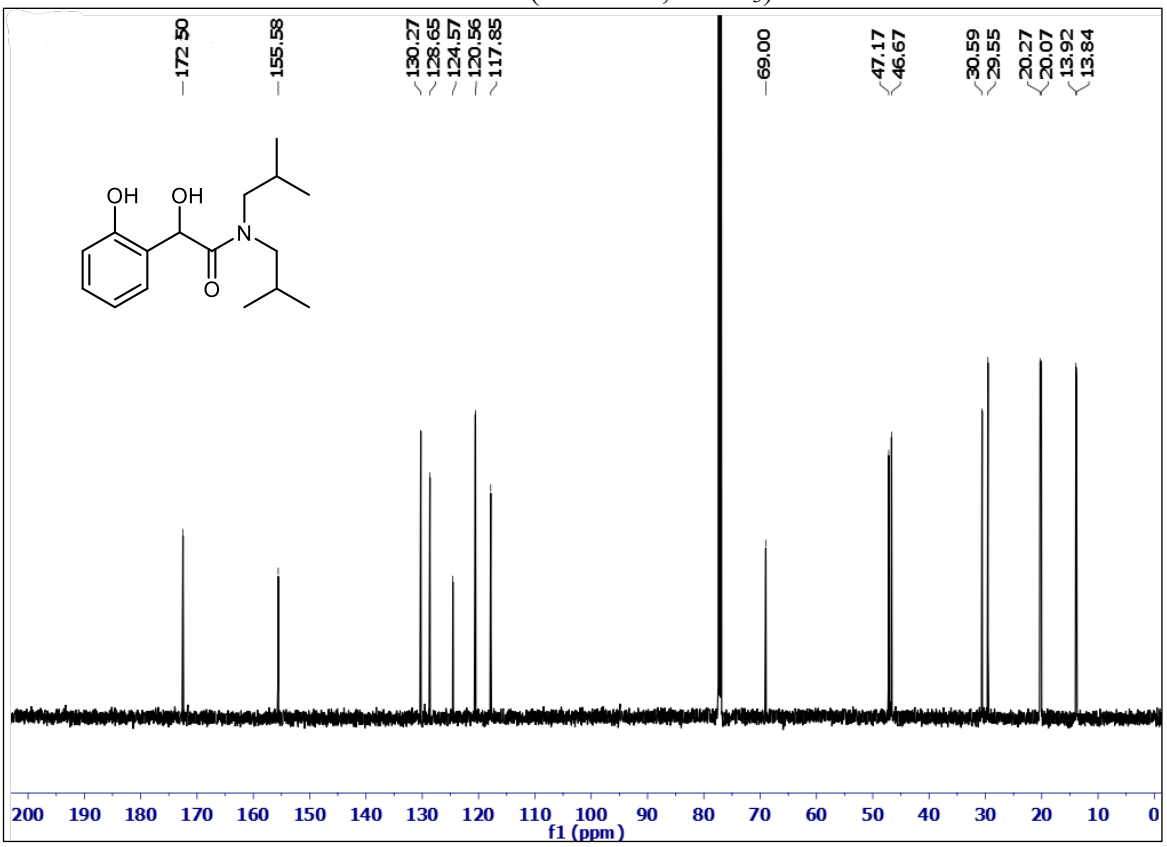


2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-diisobutylacetamide (3v)

^{1}H NMR (600 MHz, $CDCl_3$)

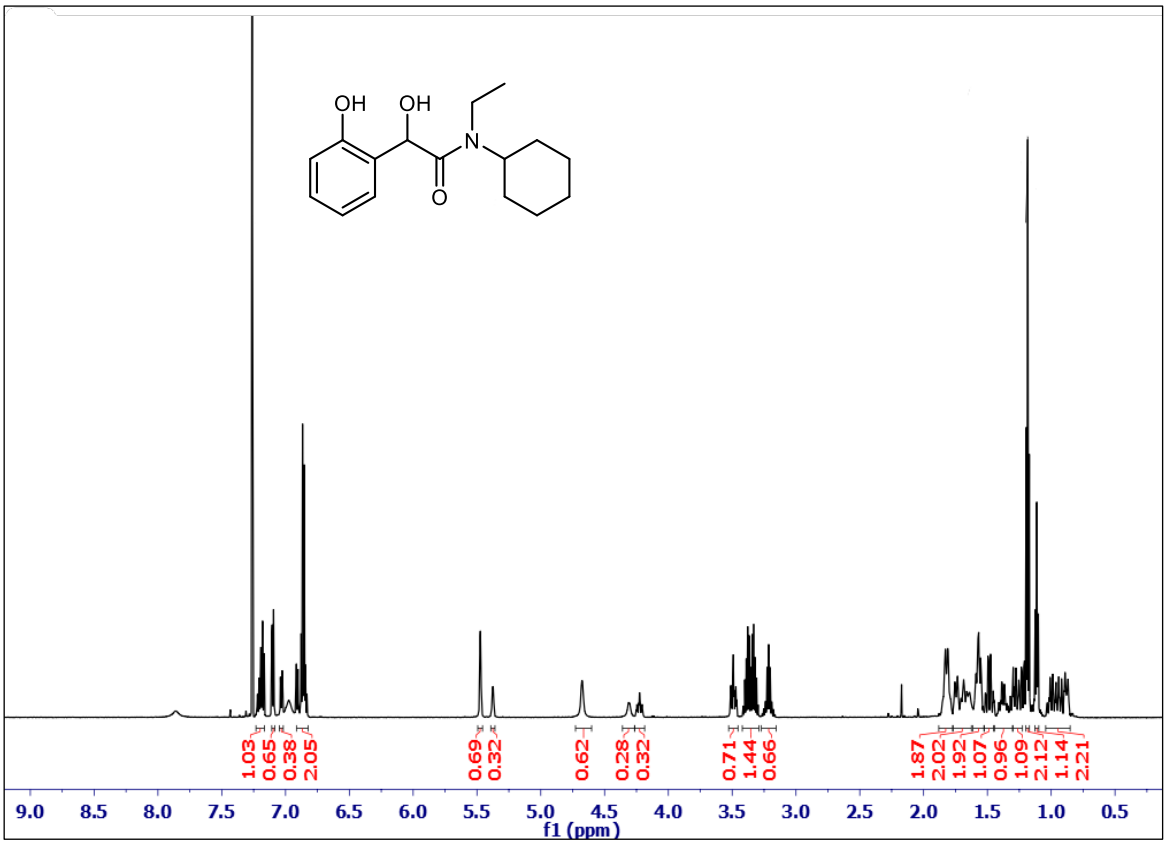


^{13}C NMR (150 MHz, $CDCl_3$)

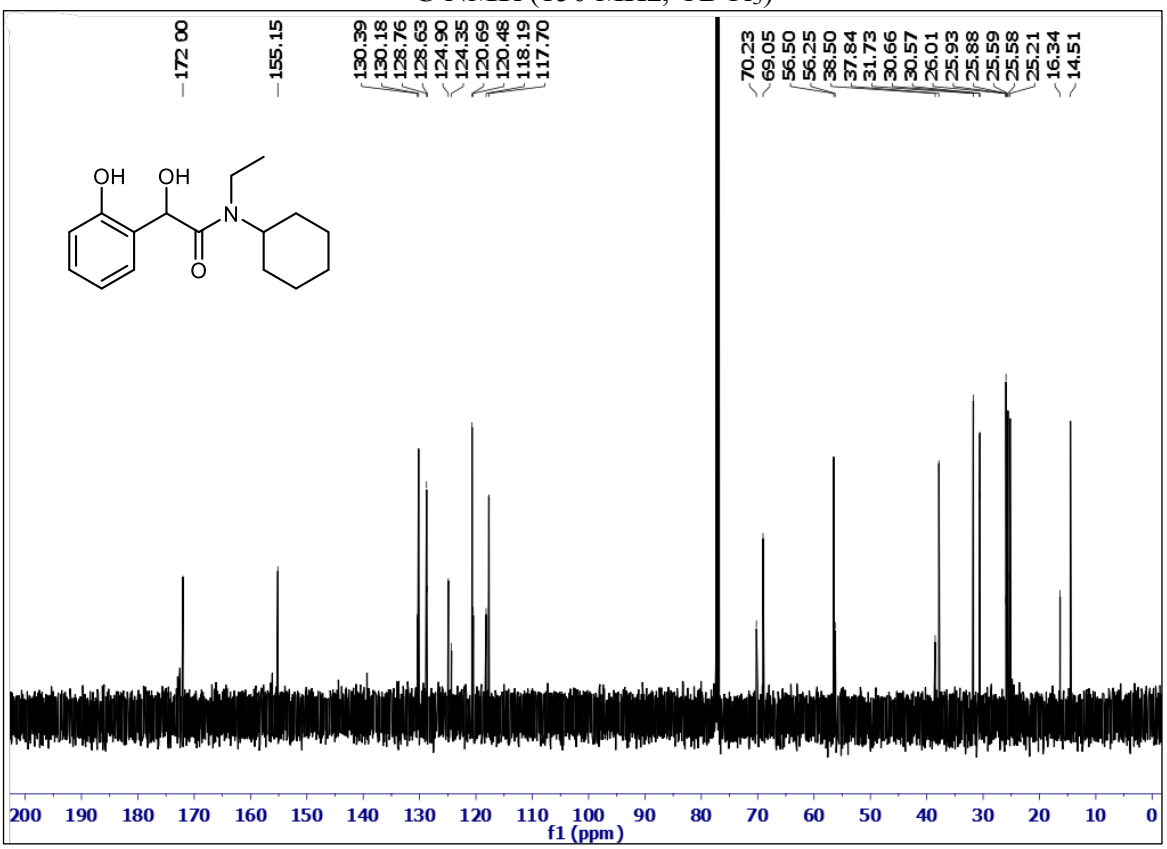


2-Hydroxy-2-(2-hydroxyphenyl)-*N*-cyclohexyl-*N*'-ethyl-acetamide (3w)

^{1}H NMR (600 MHz, $CDCl_3$)

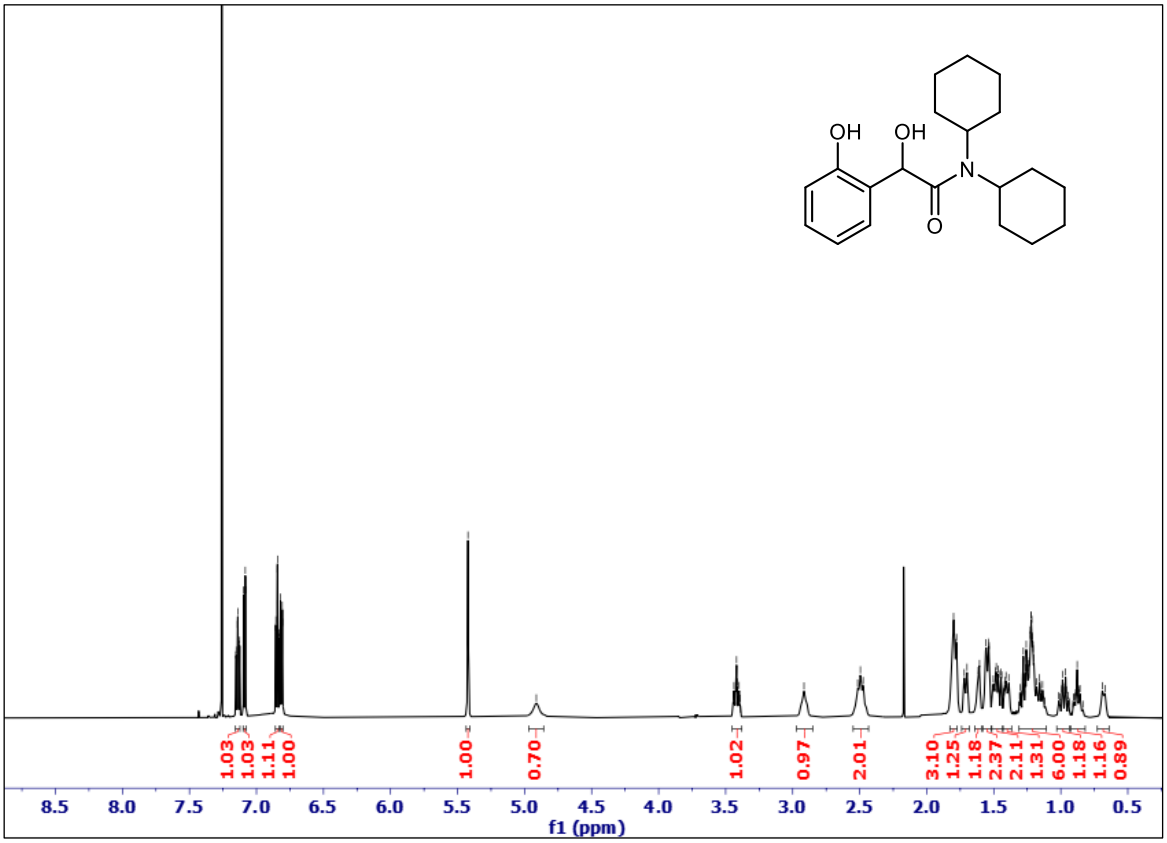


^{13}C NMR (150 MHz, $CDCl_3$)

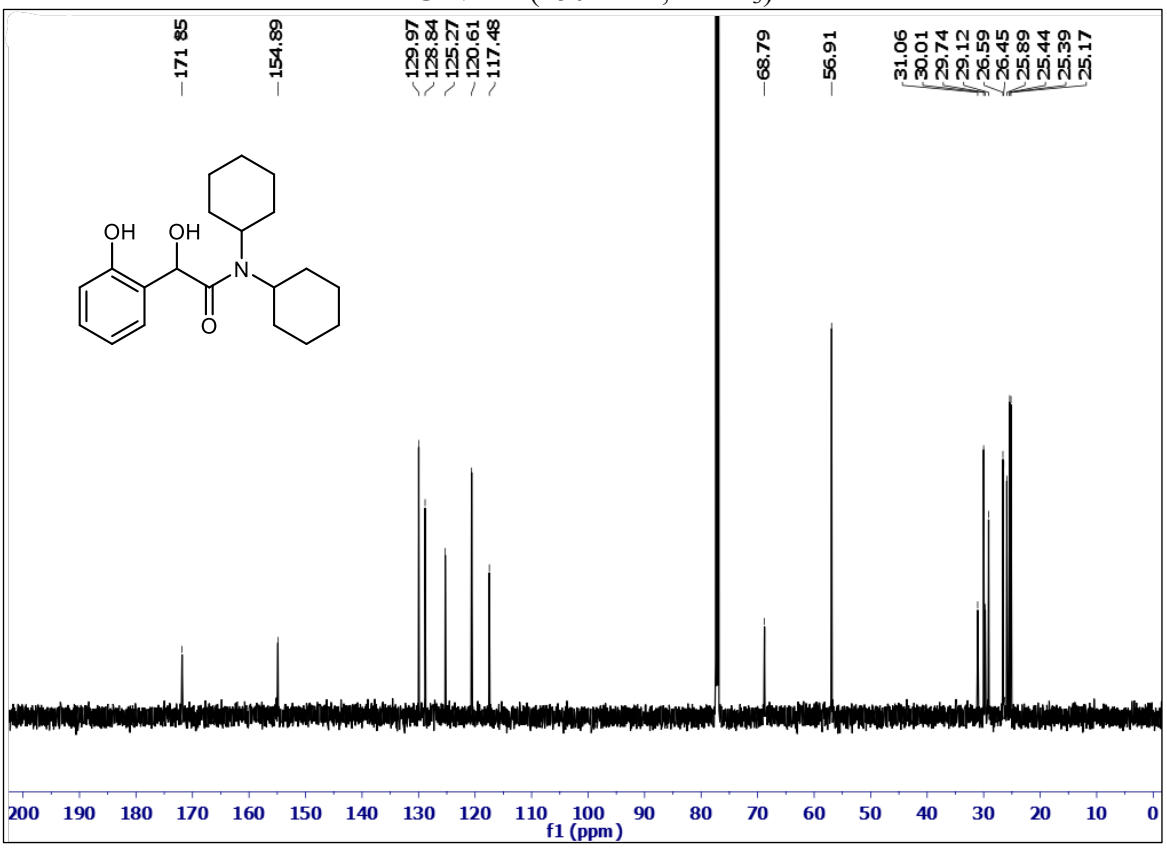


***N,N'*-Dicyclohexyl-2-hydroxy-2-(2-hydroxyphenyl)acetamide (3x)**

^{1}H NMR (600 MHz, $CDCl_3$)

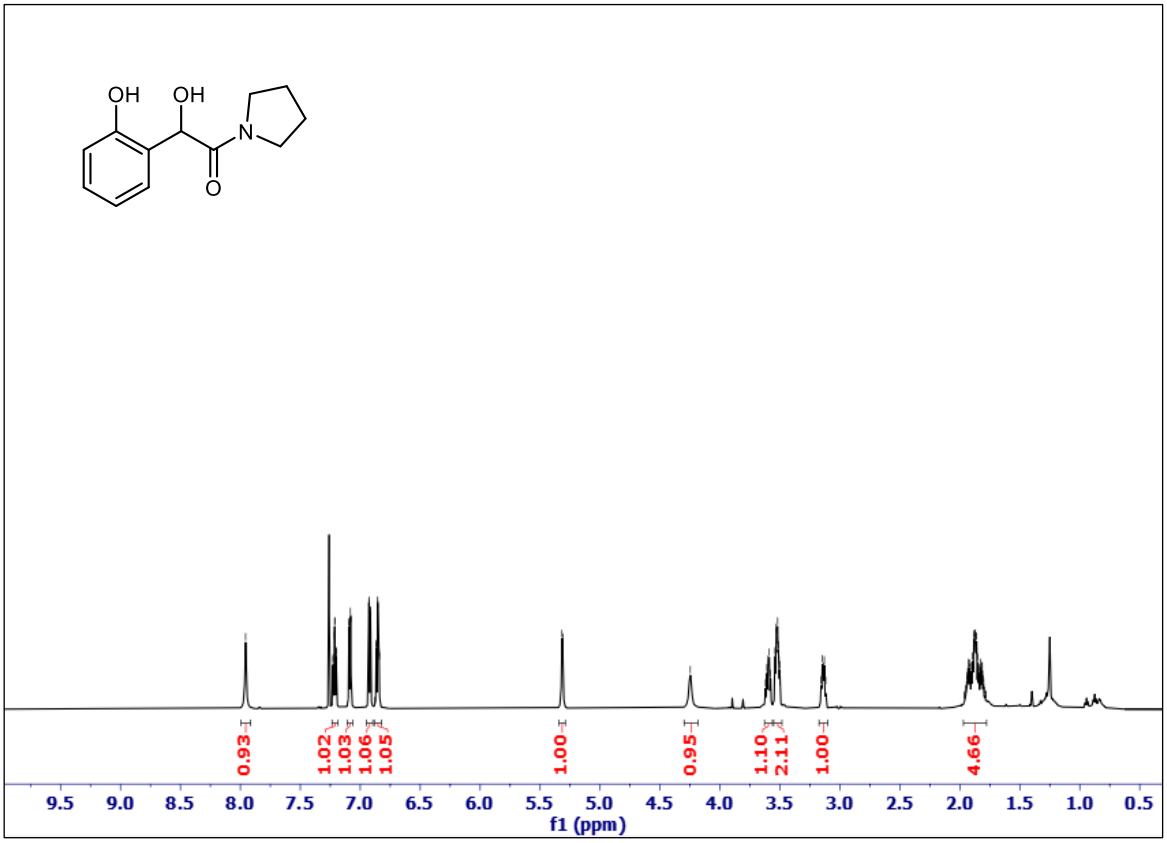


^{13}C NMR (150 MHz, $CDCl_3$)

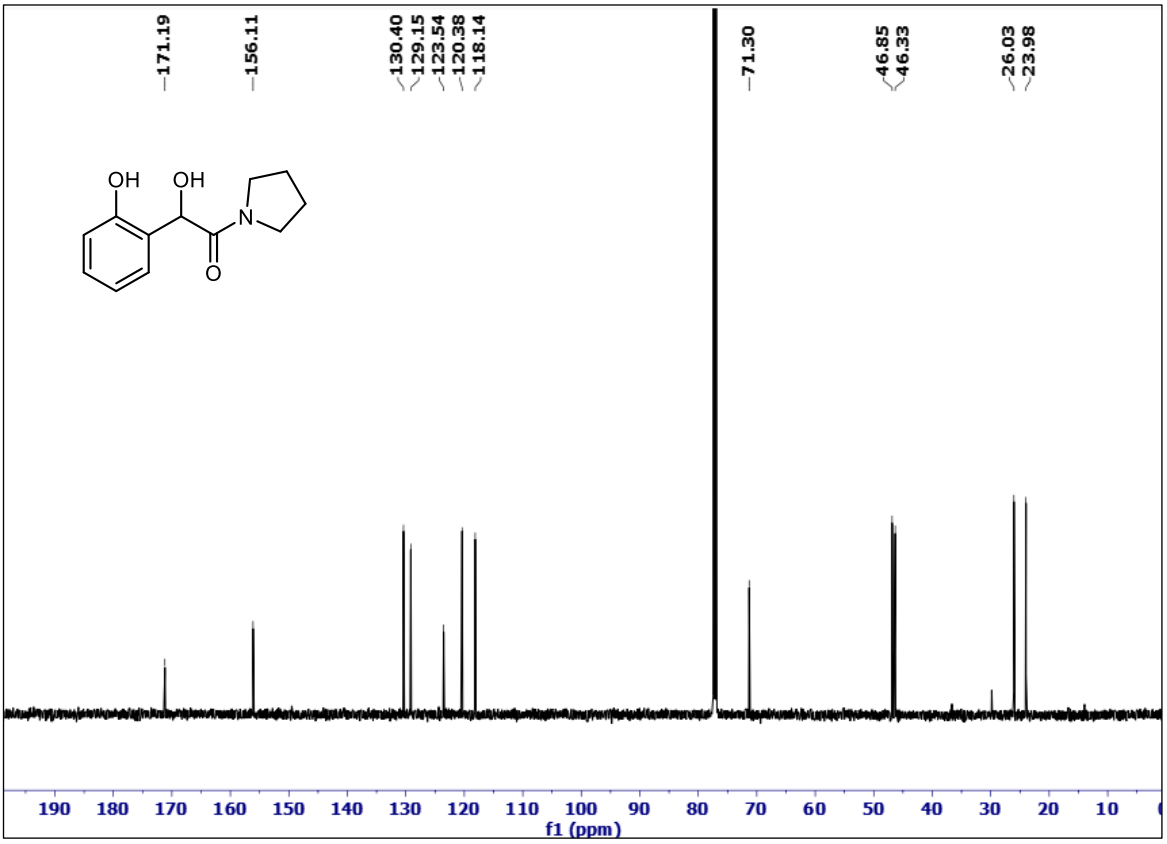


2-Hydroxy-2-(2-hydroxyphenyl)-1-(pyrrolidin-1-yl)ethan-1-one (3y)

^{1}H NMR (600 MHz, $CDCl_3$)

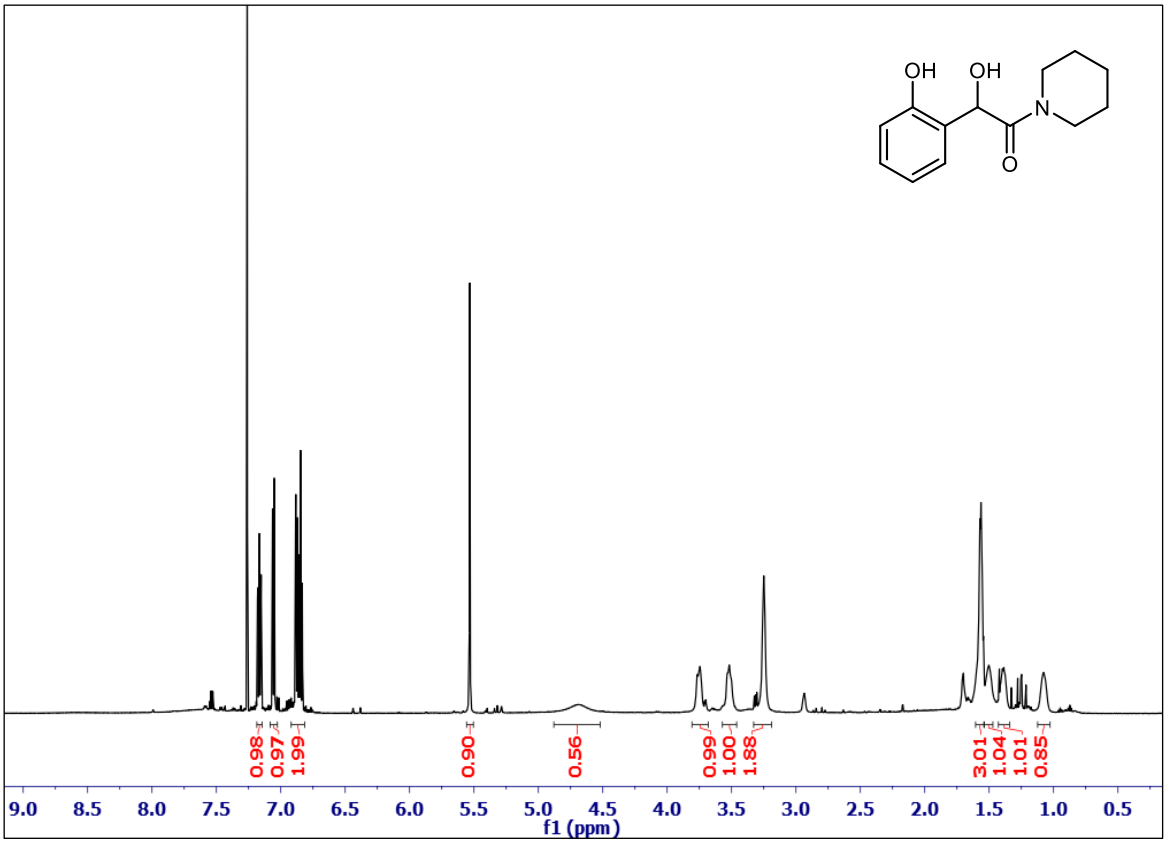


^{13}C NMR (150 MHz, $CDCl_3$)

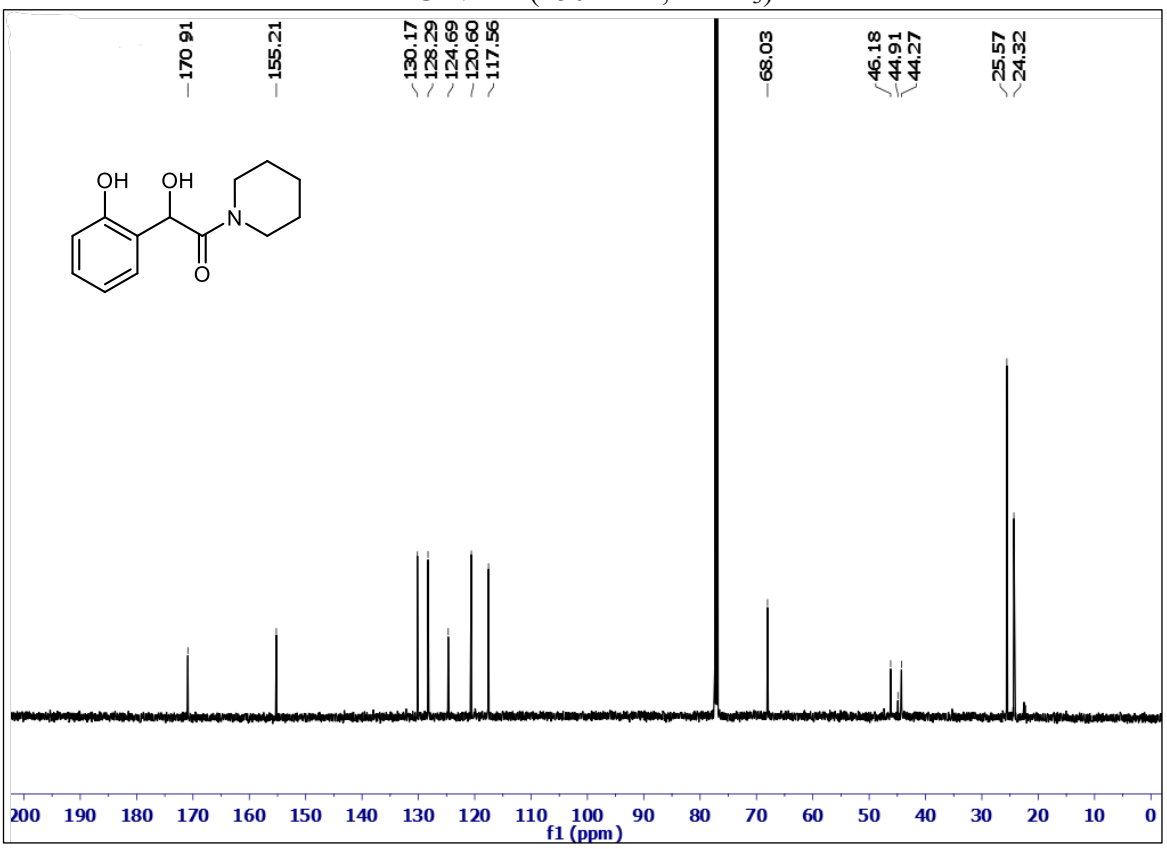


2-Hydroxy-2-(2-hydroxyphenyl)-1-(piperidin-1-yl)ethan-1-one (3z)

^{1}H NMR (600 MHz, $CDCl_3$)

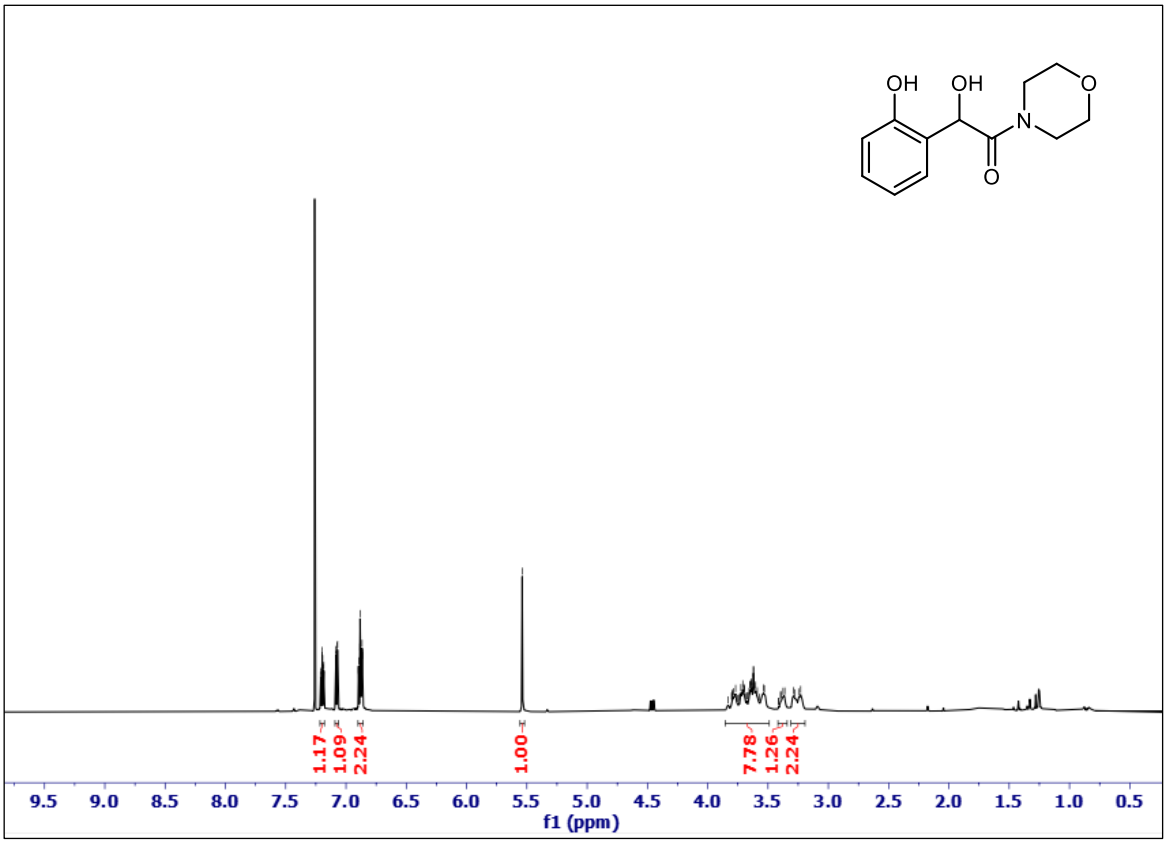


^{13}C NMR (150 MHz, $CDCl_3$)

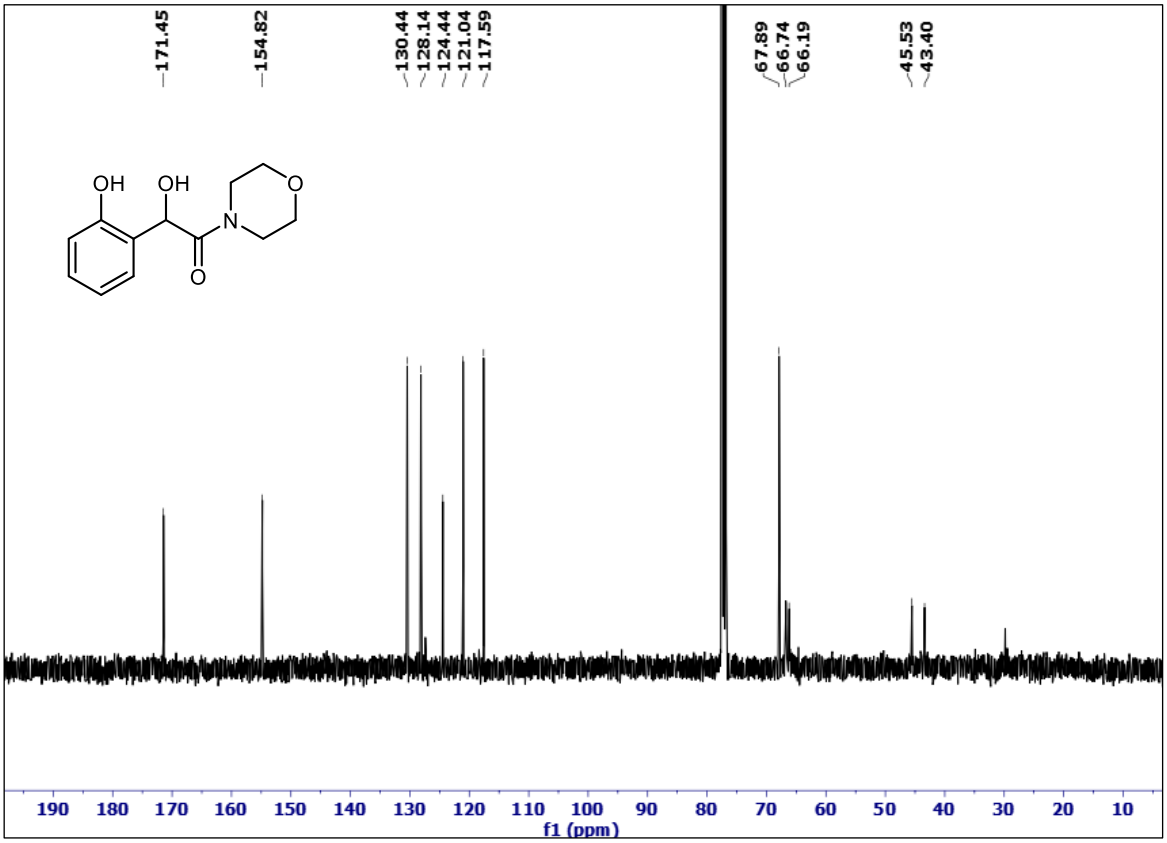


2-Hydroxy-2-(2-hydroxyphenyl)-1-morpholinoethan-1-one (3aa)

^{1}H NMR (600 MHz, $CDCl_3$)

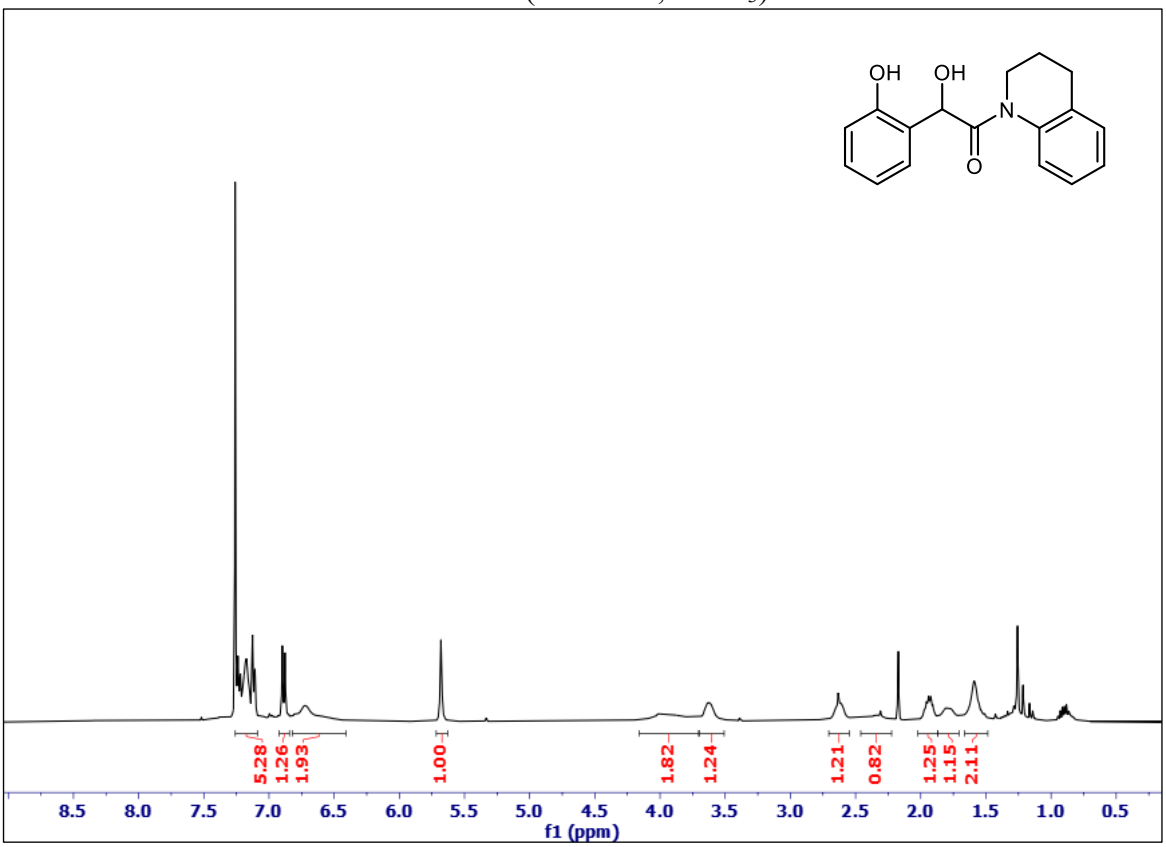


^{13}C NMR (100 MHz, $CDCl_3$)

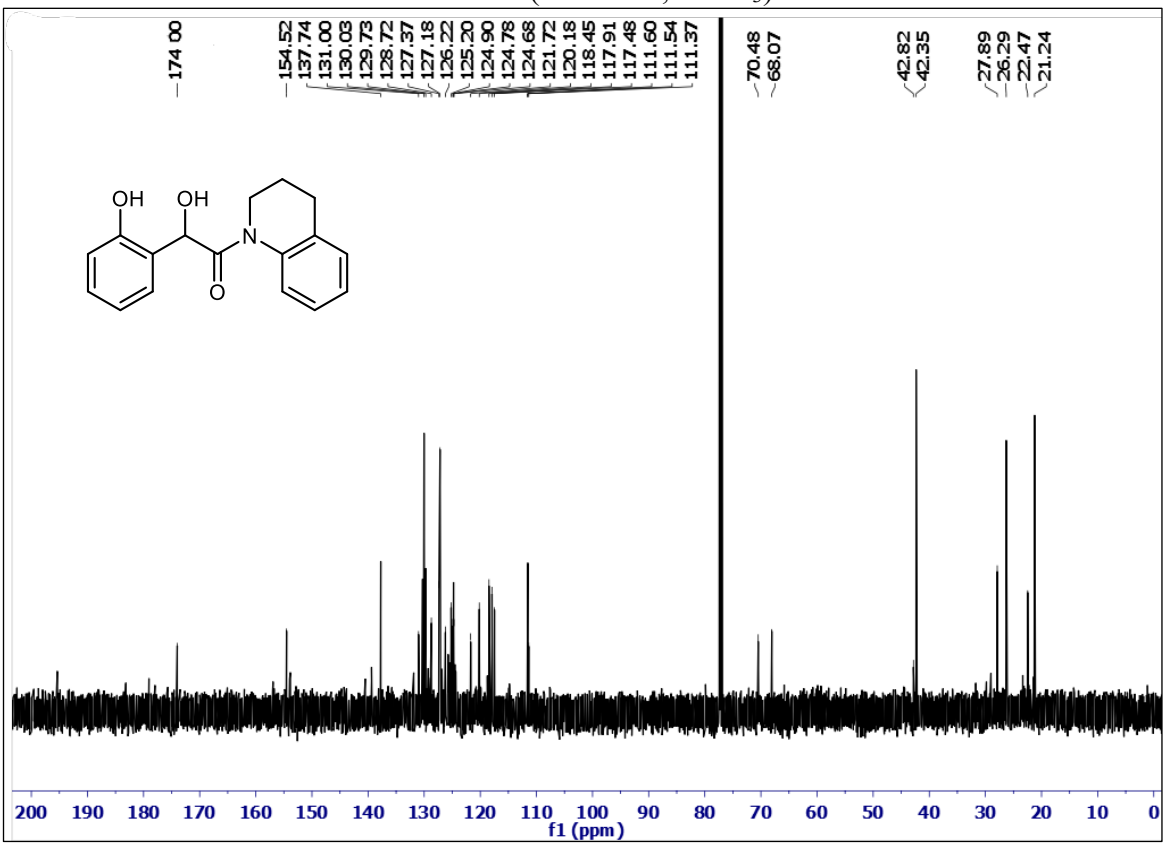


1-(3,4-Dihydroquinolin-1(2*H*)-yl)-2-hydroxy-2-(2-hydroxyphenyl)ethan-1-one (3ab)

^{1}H NMR (400 MHz, $CDCl_3$)

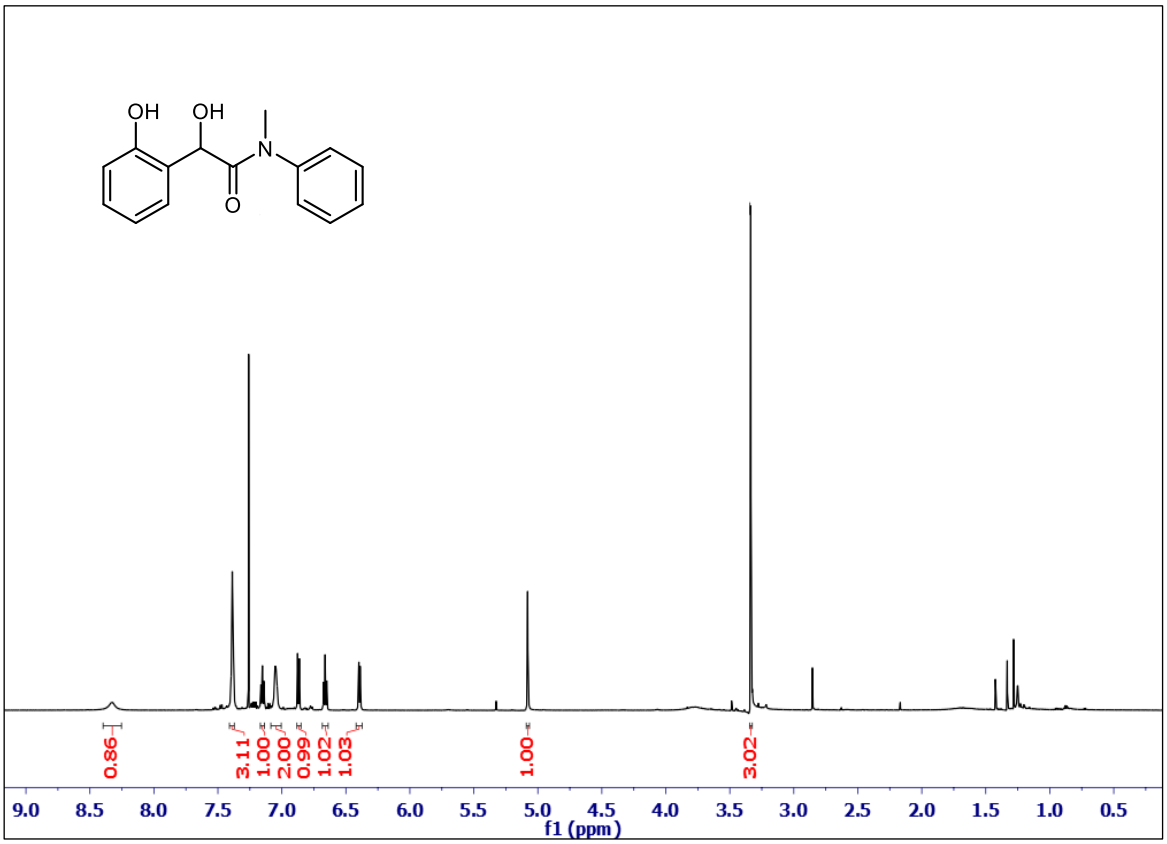


^{13}C NMR (150 MHz, $CDCl_3$)

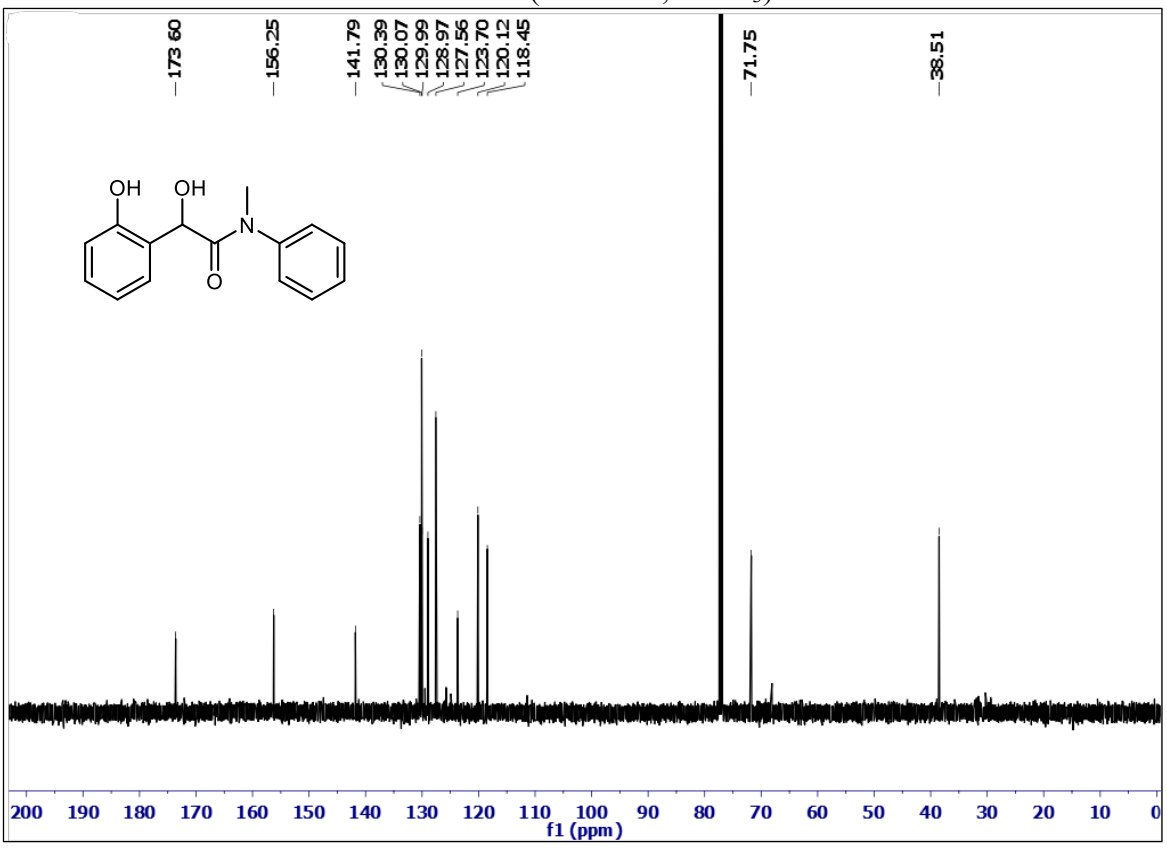


2-Hydroxy-2-(2-hydroxyphenyl)-*N*-methyl-*N*'-phenylacetamide (3ac)

^{1}H NMR (600 MHz, $CDCl_3$)

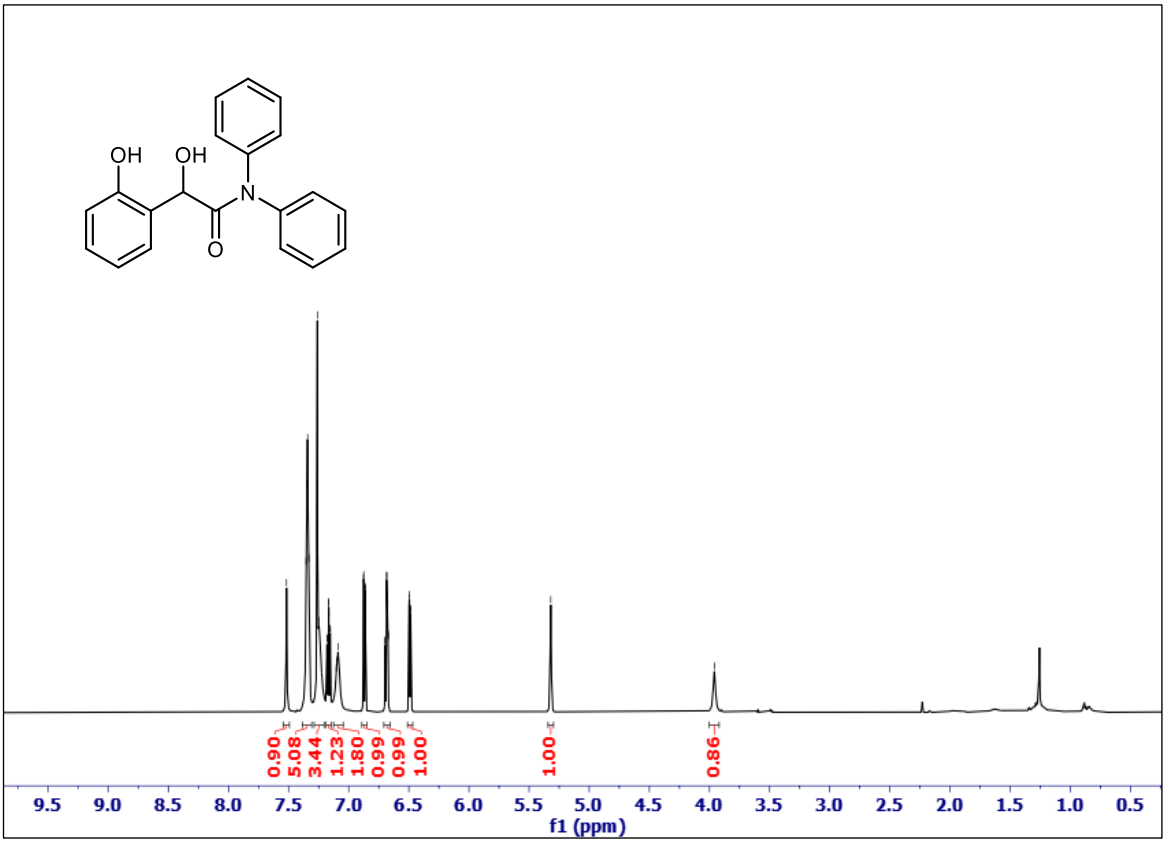


^{13}C NMR (150 MHz, $CDCl_3$)

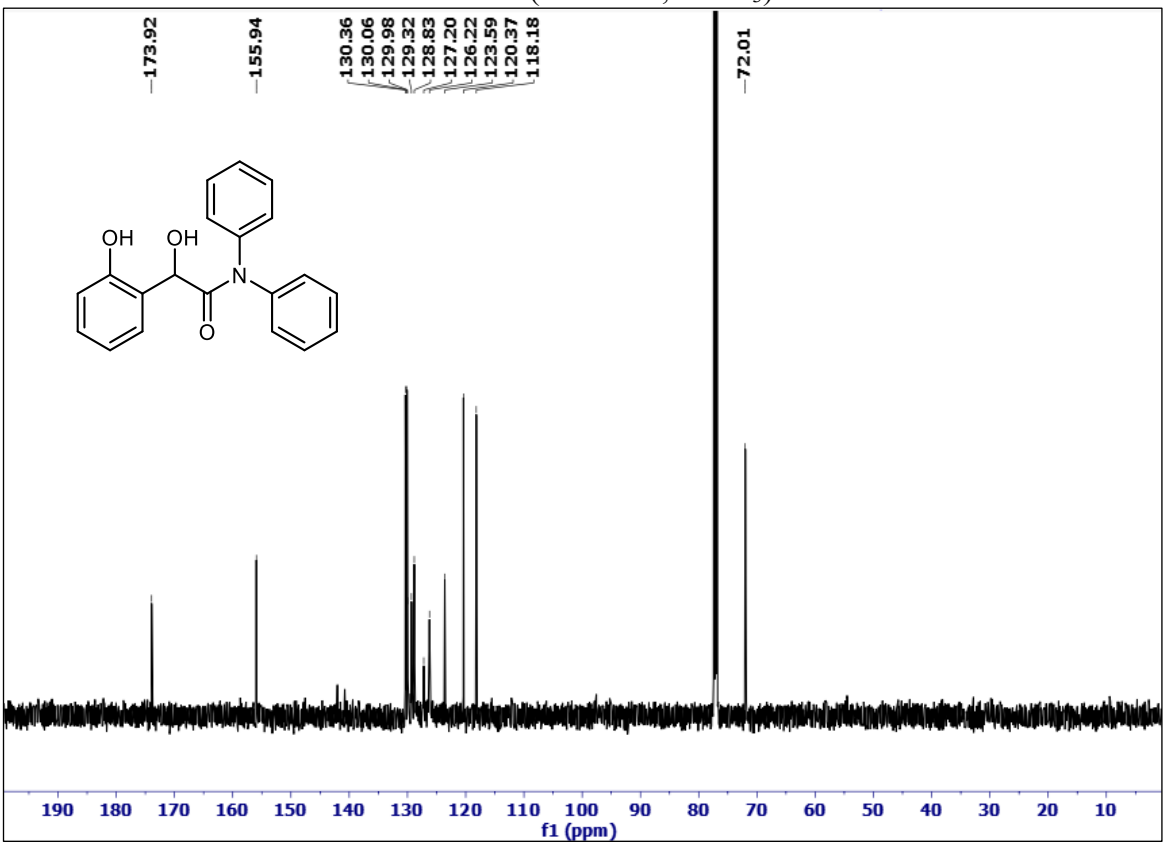


2-Hydroxy-2-(2-hydroxyphenyl)-*N*,*N*-diphenylacetamide (3ad)

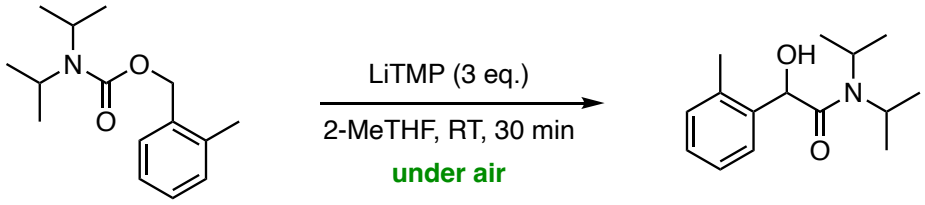
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

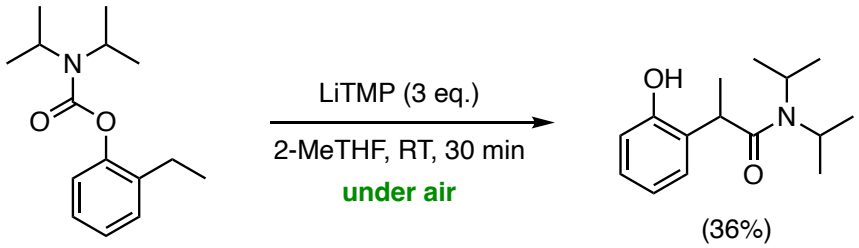


Substrate limitations



1r (88%)

2-Hydroxy-*N,N*-diisopropyl-2-(*o*-tolyl)acetamide: general procedure from **1r** (1.0 eq., 0.2 mmol, 50 mg) and LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) in 2-MeTHF (1 mL); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 95/5 v/v) gave 2-hydroxy-*N,N*-diisopropyl-2-(*o*-tolyl)acetamide as a white solid (44 mg, 88%, R_f = 0.18 petroleum ether/EtOAc 95/5 v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.14 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 1H), 5.26 (d, *J* = 5.6 Hz, 1H), 4.95 (d, *J* = 5.6 Hz, 1H), 3.54 (sept, *J* = 6.7 Hz, 1H), 3.38 (sept, *J* = 6.8 Hz, 1H), 2.46 (s, 3H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 138.2, 136.2, 131.2, 128.5, 127.2, 126.7, 69.1, 48.1, 46.5, 20.7, 20.7, 19.9, 19.2, 18.7.

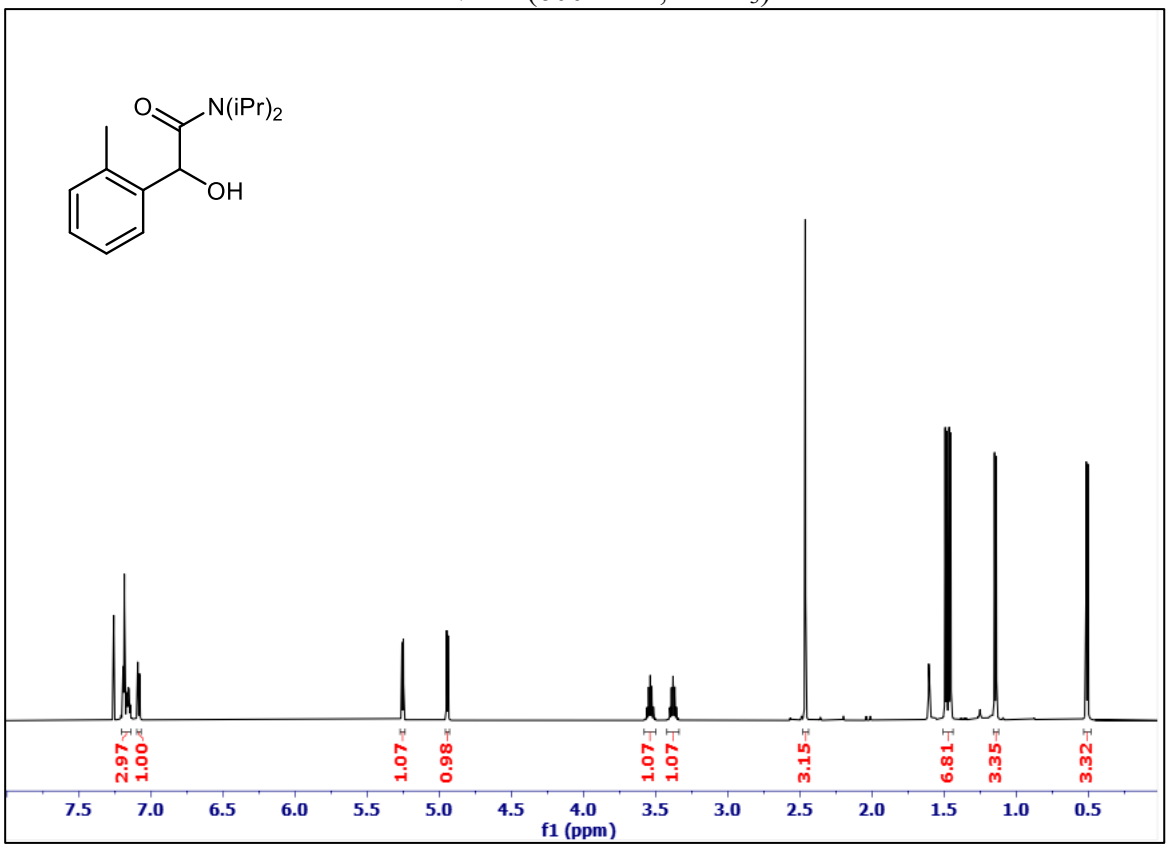


(36%)

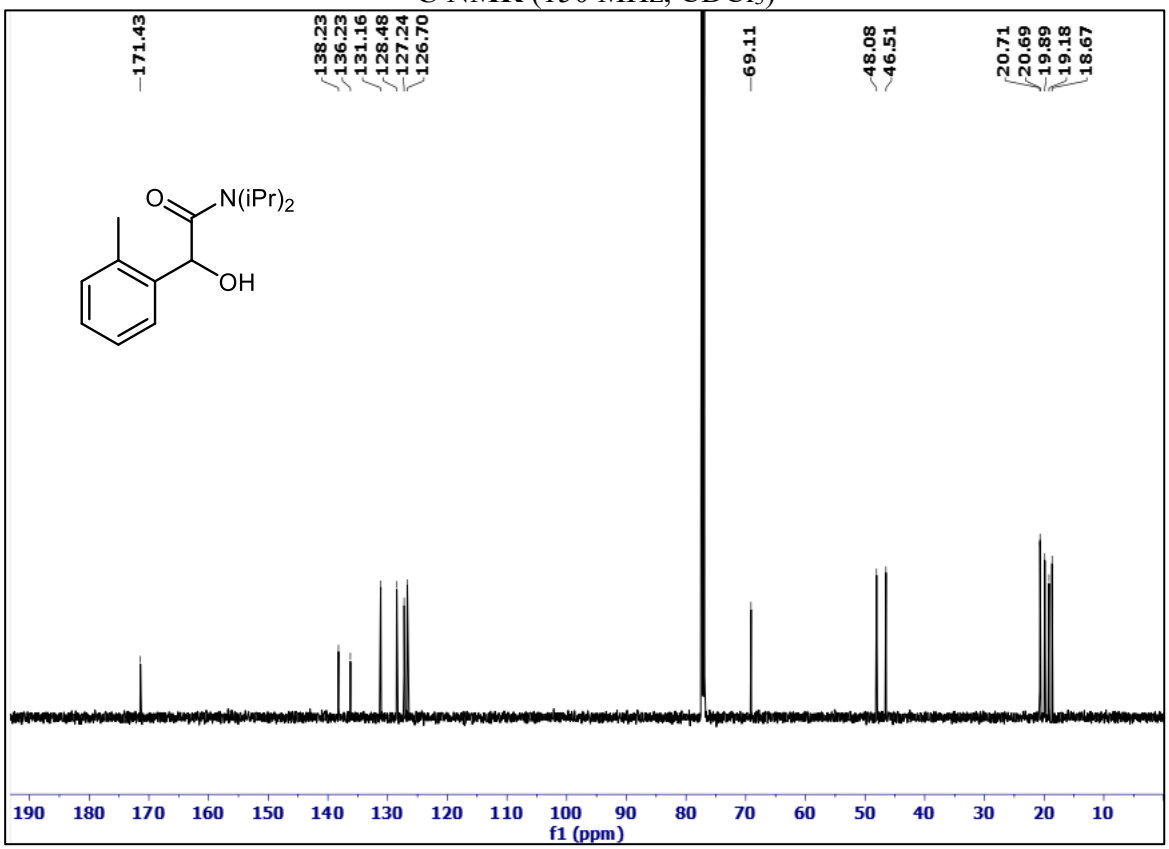
2-(2-Hydroxyphenyl)-*N,N*-diisopropylpropanamide: general procedure from *O*-2-ethylphenyl *N,N*-diisopropylcarbamate[10] (1.0 eq., 0.2 mmol, 50 mg) and LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.6 mL) in 2-MeTHF (1 mL); purification by flash column chromatography on silica gel (petroleum ether/EtOAc 90/10 v/v) gave 2-(2-hydroxyphenyl)-*N,N*-diisopropylpropanamide as a white solid (18 mg, 36%, R_f = 0.30 petroleum ether/EtOAc 90/10 v/v) and unreacted *O*-2-ethylphenyl *N,N*-diisopropylcarbamate as a colourless oil (26 mg, 52%, R_f = 0.70 petroleum ether/EtOAc 90/10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (br s, 1H), 7.14 (td, *J* = 7.8, 1.7 Hz, 1H), 6.98 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 4.27-4.11 (m, 1H), 3.95 (q, *J* = 7.2 Hz, 1H), 3.84-3.55 (m, 1H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 3H), 1.32 (d, *J* = 6.8 Hz, 6H), 1.13 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.3, 157.0, 130.3, 128.8, 126.0, 119.7, 118.8, 46.7, 21.7, 21.2, 20.6, 20.4, 17.9.

2-Hydroxy-*N*,*N*-diisopropyl-2-(*o*-tolyl)acetamide

^{1}H NMR (600 MHz, $CDCl_3$)

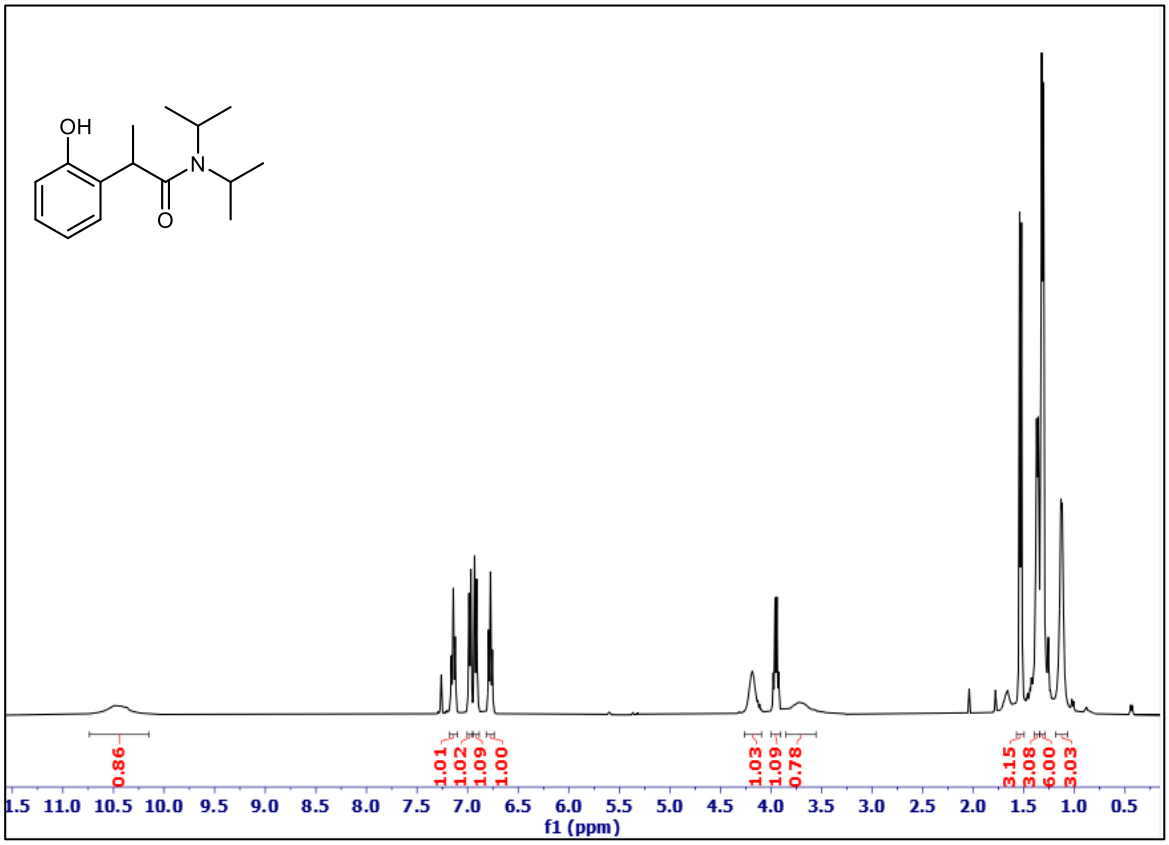


^{13}C NMR (150 MHz, $CDCl_3$)

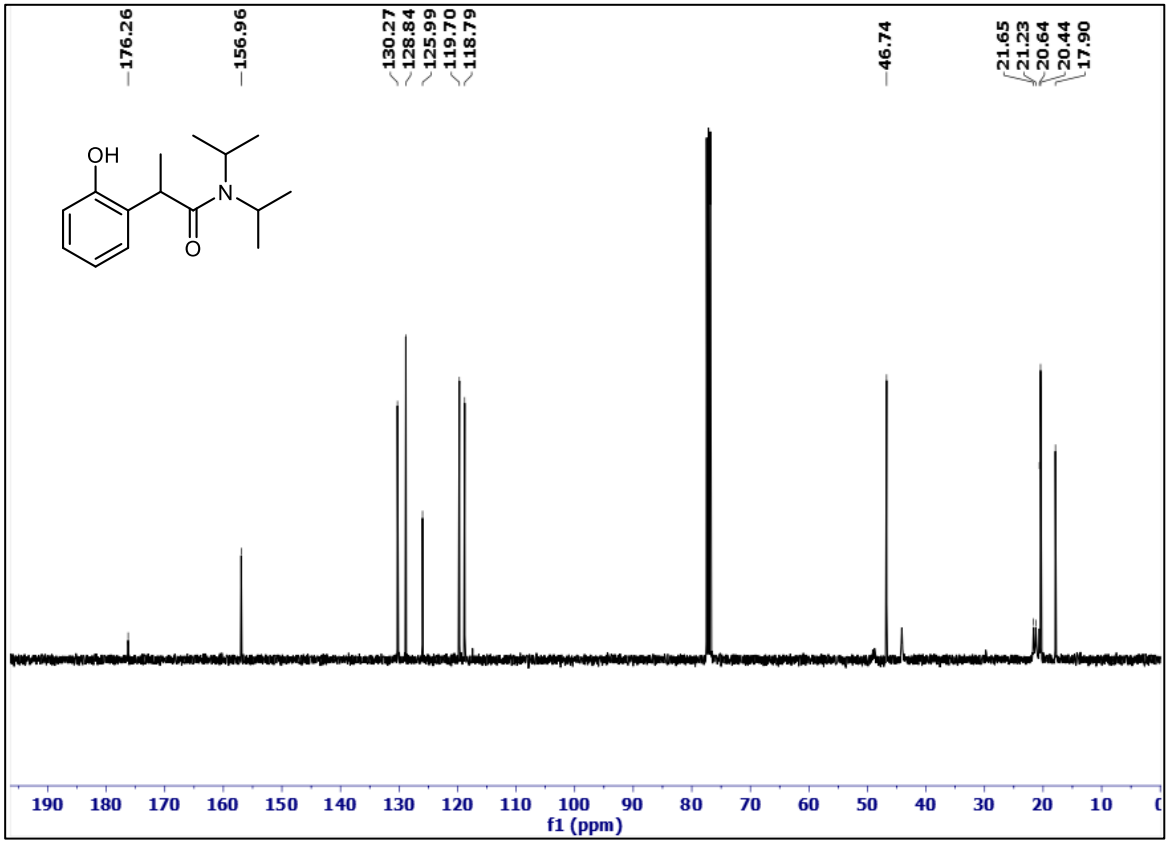


2-(2-Hydroxyphenyl)-*N*,*N*-diisopropylpropanamide

^{1}H NMR (400 MHz, $CDCl_3$)

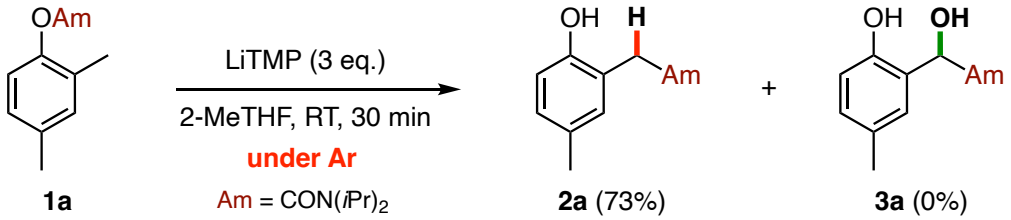


^{13}C NMR (100 MHz, $CDCl_3$)



Mechanistic investigations

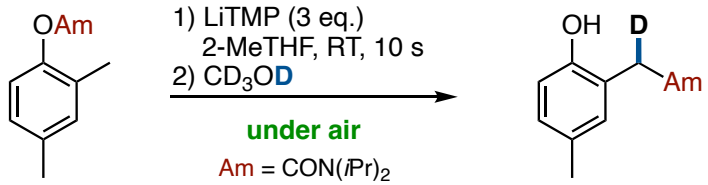
*Rearrangement of carbamate **1a** under inert atmosphere*



1a **2a** (73%) **3a** (0%)

To a stirred solution of **1a** (0.20 mmol, 50 mg) under a positive pressure of argon in previously degassed 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) was added at room temperature. The resulting reaction mixture was stirred for 30 min and then quenched with 2 M HCl. The aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 9/1 v/v) gave **2a** as a white solid (37 mg, 73%). The product **3a** was not detected.

*Deuterium-labelling experiment: synthesis and analysis of **2a-D***

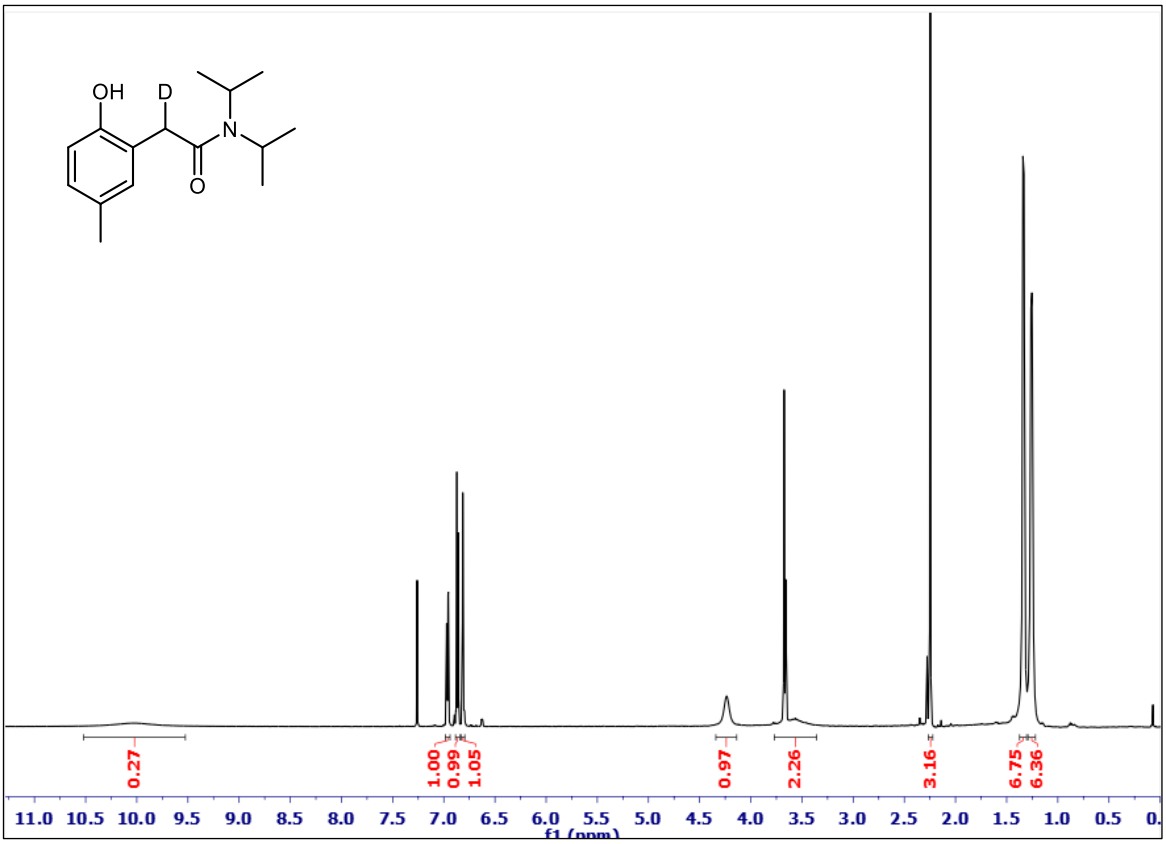


1a **2a-D** (60%, 73% D)

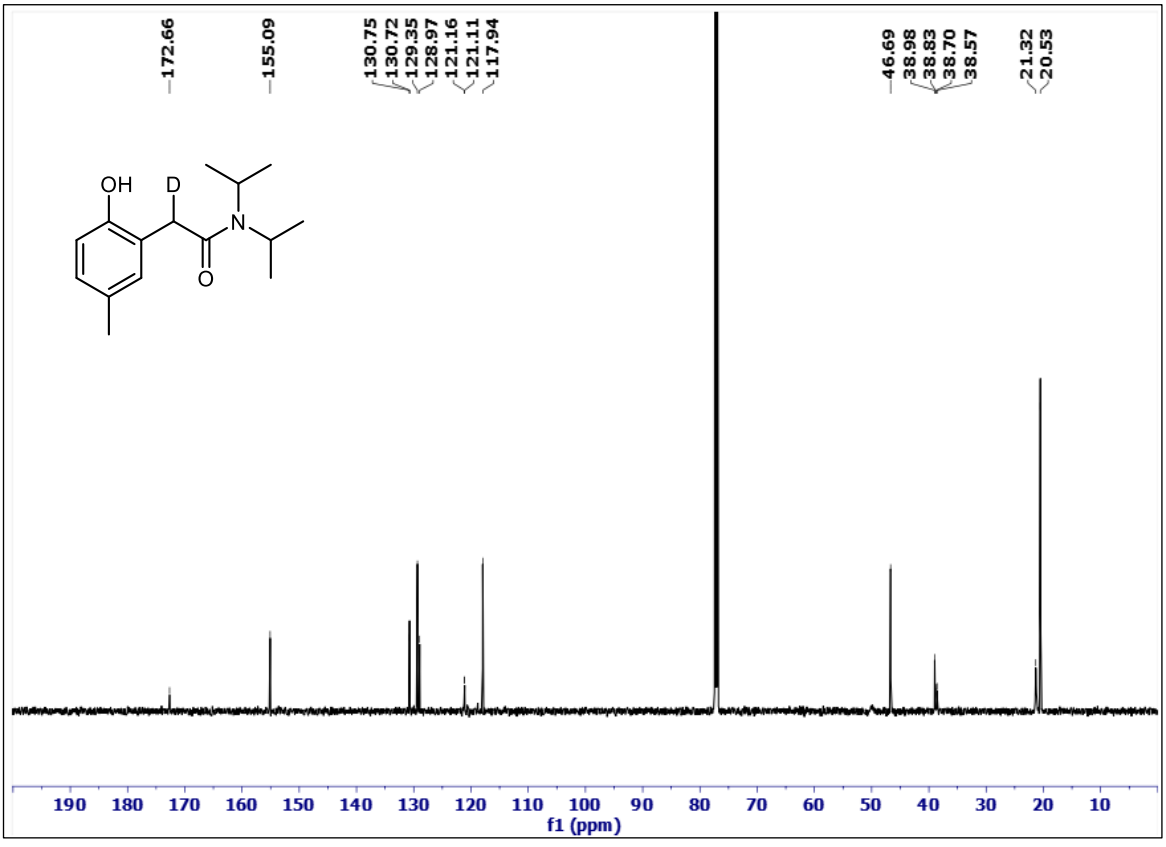
2-Deuterio-2-(2-hydroxy-5-methylphenyl)-*N*,*N*-diisopropylacetamide (2a-D): To a stirred solution of **1a** (0.50 mmol, 0.12 g) in 2-MeTHF (5 mL) under air, LiTMP (3.0 eq., 1 M in 2-MeTHF) was added at room temperature. The resulting reaction mixture was stirred for 10 s, then CD_3OD was added and stirred for 10 min. Water was added, the mixture was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The resulting crude material was purified by flash column chromatography on silica gel (petroleum ether/EtOAc 9/1 v/v) to give **2a-D** as a white solid (72 mg, 60%, R_f = 0.21 petroleum ether/EtOAc 9/1 v/v, 73% D), mp. 163.0-165.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (br s, 1H), 6.96 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 4.24 (br s, 1H), 3.67 (d, *J* = 9.9 Hz, 1H) superimposed to 3.57 (br s, 1H), 2.25 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.26 (d, *J* = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 172.7, 155.1, 130.7, 129.4, 129.0, 121.1, 117.9, 46.7, 39.0, 38.7 (t, *J* = 19.2 Hz, 1C), 21.3, 20.5. ^{2}H NMR (92.07 MHz, CH_2Cl_2) δ 3.64 (d, *J* = 2.1 Hz, 1D). HRMS (ESI): *m/z* calcd for $C_{15}H_{22}DNO_2$ + Na $^+$: 273.1684 [M+Na$^+$]; found 273.1690.

2-Deuterio-2-(2-hydroxy-5-methylphenyl)-*N*,*N*-diisopropylacetamide (2a-D)

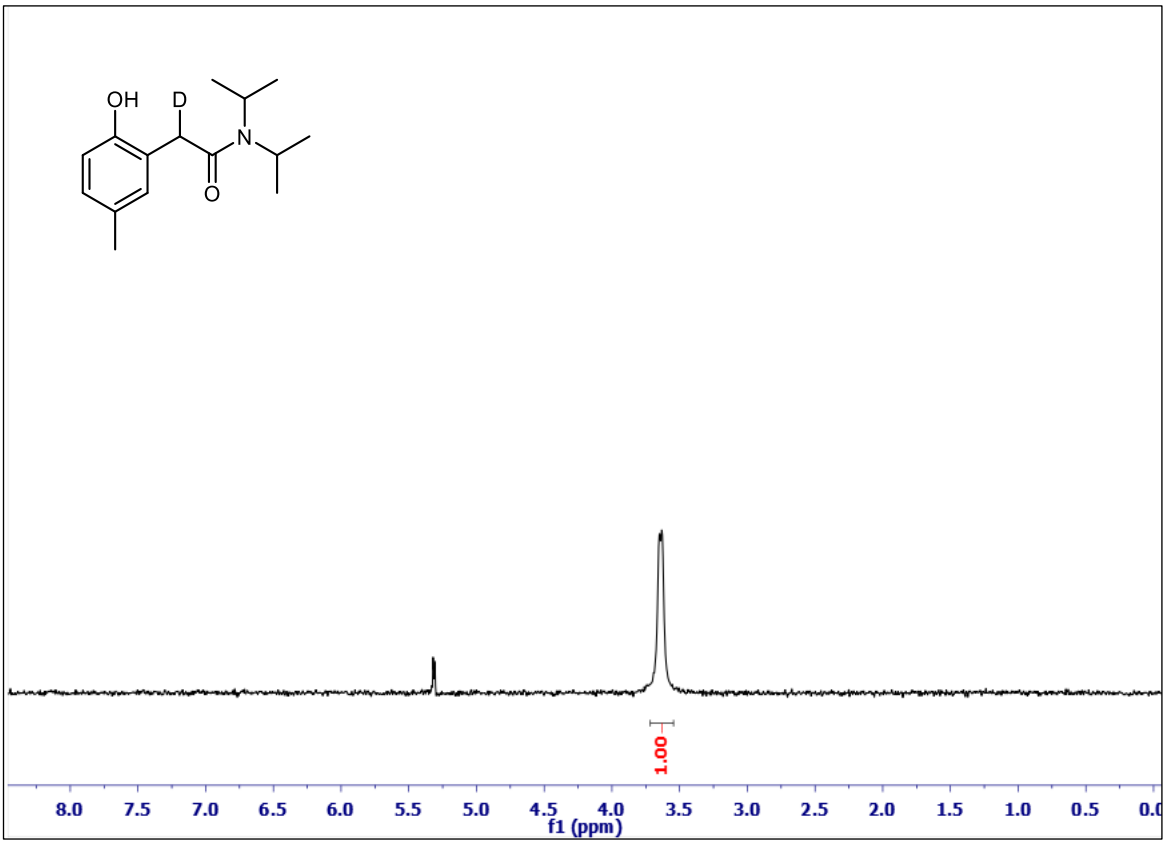
^{1}H NMR (600 MHz, $CDCl_3$)



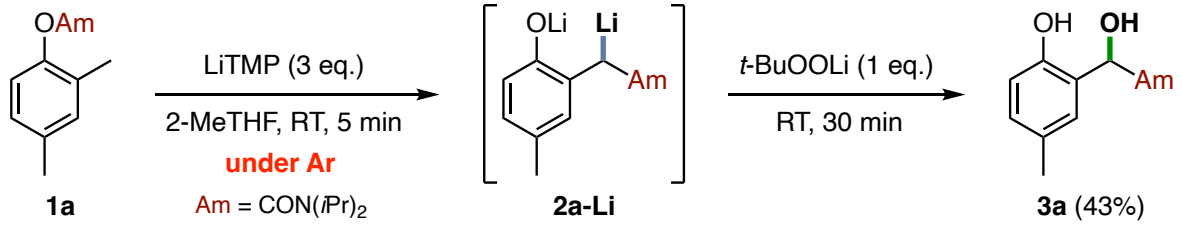
^{13}C NMR (150 MHz, $CDCl_3$)



^{2}H NMR (92.07 MHz, CH_2Cl_2)



*Oxidation of enolate **2a-Li** promoted by t-BuOOLi*



1a **2a-Li** **3a** (43%)

To a stirred solution of **1a** (0.20 mmol, 50 mg) under a positive pressure of argon in previously degassed 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) was added at room temperature. The mixture was stirred for 5 min, then *t*-BuOOLi (1.0 eq., 0.5 M in 2-MeTHF, 0.20 mmol, 0.4 mL)[11] was added at room temperature, the resulting reaction mixture was stirred for 30 min and then quenched with 2 M HCl. The aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The yield of **3a** (43%) was determined by quantitative ^{1}H NMR in CD_3OD using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor of 1 for the preparation of the sample (See Eq. 1).

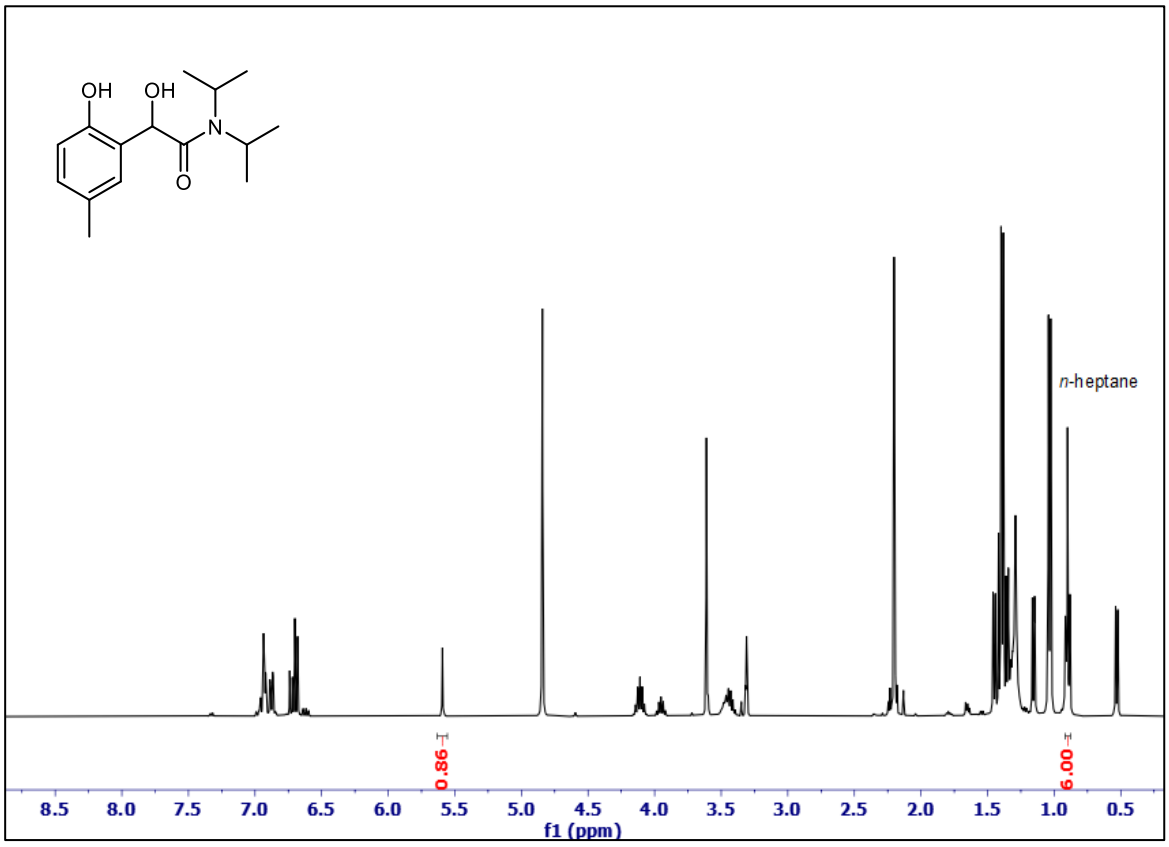
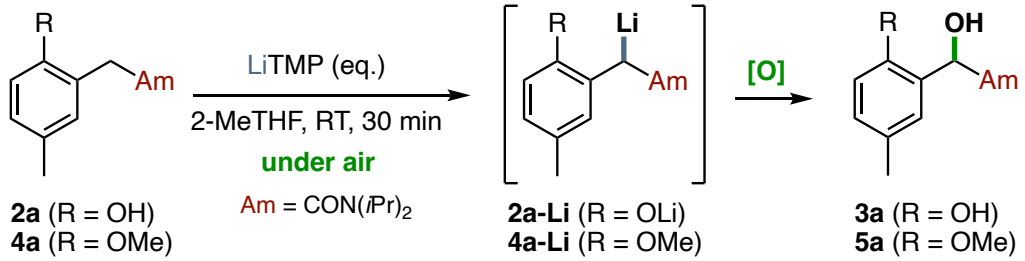


Figure S4: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **1a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mL) at RT, then t-BuOOLi (1 eq.). Yield **3a**: 43%.

*Enolization/aerobic oxidation of arylacetamides **2a** and **4a***



2a (R = OH)
4a (R = OMe)

2a-Li (R = OLi)
4a-Li (R = OMe)

3a (R = OH)
5a (R = OMe)

entry	substrate	LiTMP (eq.)	Product (Yield %)[a]	
1	**2a**	1	**2a** (81)	**3a** (6)
2	**2a**	2	**2a** (3)	**3a** (60)
3	**4a**	1	**4a** (30)	**5a** (45)
4	**4a**	2	**4a** (0)	**5a** (63)

General procedure. To a stirred solution of **2a** or **4a** (1.0 eq., 0.20 mmol) in 2-MeTHF (1 mL), the selected amount of LiTMP (1 M in 2-MeTHF) was added at room temperature. The resulting reaction mixture was stirred for 30 min under air and then quenched with 2 M HCl. The aqueous layer was extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. [a] Yields of **2a**, **3a**, **4a** and **5a** were determined by quantitative ^{1}H NMR in CD_3OD using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor of 1 for the preparation of the sample (See Eq. 1).

*Synthesis and analysis of compounds **4a** and **5a***

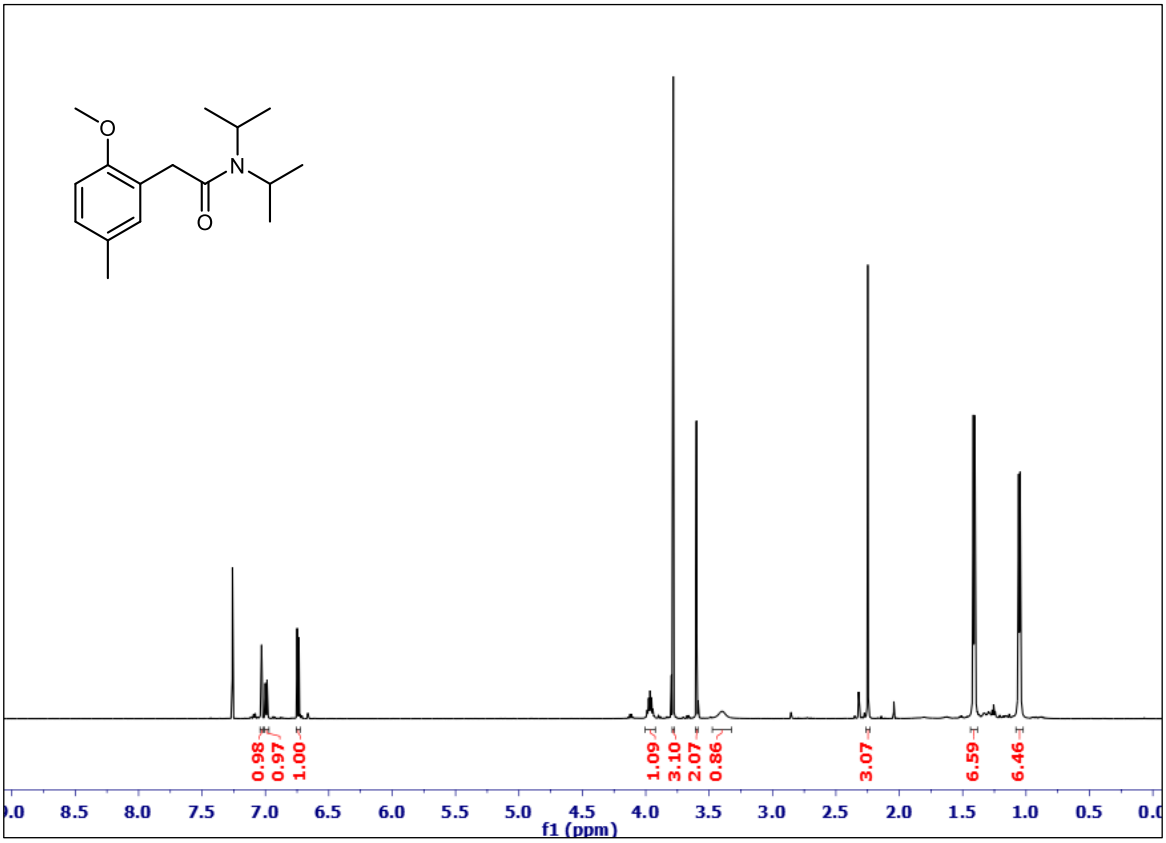
***N,N*-Diisopropyl-2-(2-methoxy-5-methylphenyl)acetamide (4a):** To a stirred solution of acetamide **2a** (1.0 eq., 1.00 mmol) in DMF (6 mL), K_2CO_3 (3.0 eq., 3.00 mmol) and iodomethane (1.2 eq., 1.20 mmol) were added. The resulting reaction mixture was stirred overnight at room temperature. The mixture was diluted with water, and extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The resulting crude material was purified by flash column chromatography on silica gel (petroleum ether/EtOAc 9/1 v/v) to give **4a** as a white solid (0.18 g, 74%, R_f = 0.28 petroleum ether/EtOAc 9/1 v/v), mp. 49.0-51.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 2.2 Hz, 1H), 6.99 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 3.97 (sept, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 2H), 3.40 (br s, 1H), 2.25 (s, 3H), 1.41 (d, *J* = 6.7 Hz, 6H), 1.05 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.7, 154.5, 130.5, 129.8, 128.0, 124.3, 110.3, 55.5, 49.0, 45.6, 36.7, 20.7, 20.6, 20.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_2 + H^+$: 264.1960 [M+H$^+$]; found 264.1965.

2-Hydroxy-*N,N*-diisopropyl-2-(2-methoxy-5-methylphenyl)acetamide (5a): General procedure starting from **4a**. Purification by flash column chromatography gave **5a** as a white solid (petroleum ether/EtOAc 8/2 v/v (R_f = 0.40 petroleum ether/EtOAc 8/2 v/v), mp. 104.0-106.0 °C. Mixture of rotamers. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.04 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.53 (d, *J* = 5.9

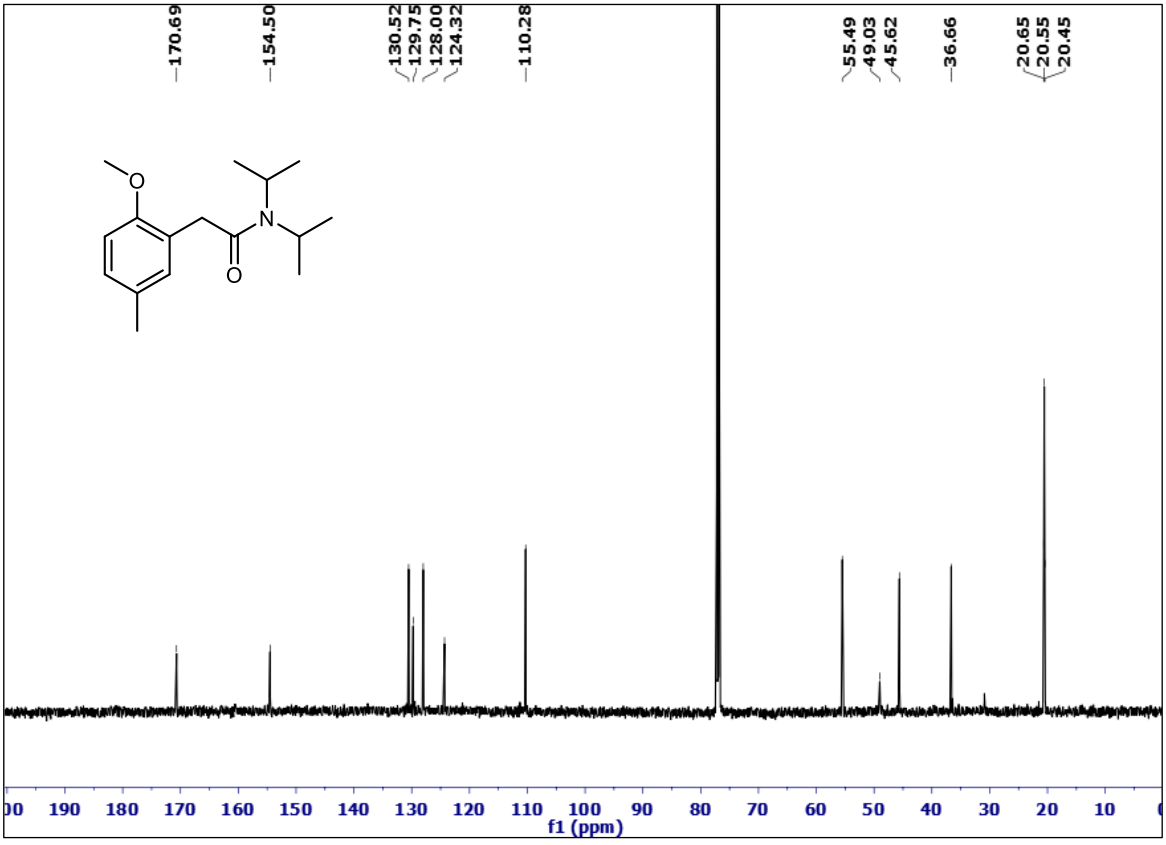
Hz, 1H), 4.99 (d, J = 5.9 Hz, 1H), 3.84 (s, 3H), 3.76 (sept, J = 6.8Hz, 1H), 3.34 (sept, J = 6.8 Hz, 1H), 2.23 (s, 3H), 1.47 (d, J = 6.8 Hz, 3H), 1.38 (d, J = 6.8 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H), 0.46 (d, J = 6.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 171.8, 154.4, 130.6, 130.0, 128.7, 128.4, 111.2, 65.0, 56.0, 47.5, 46.3, 20.8, 20.6, 20.4, 19.7, 18.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_3 + Na^+$: 302.1730 [M+Na^+]; found 302.1735.

***N*,*N*-Diisopropyl-2-(2-methoxy-5-methylphenyl)acetamide (4a)**

^{1}H NMR (600 MHz, $CDCl_3$)

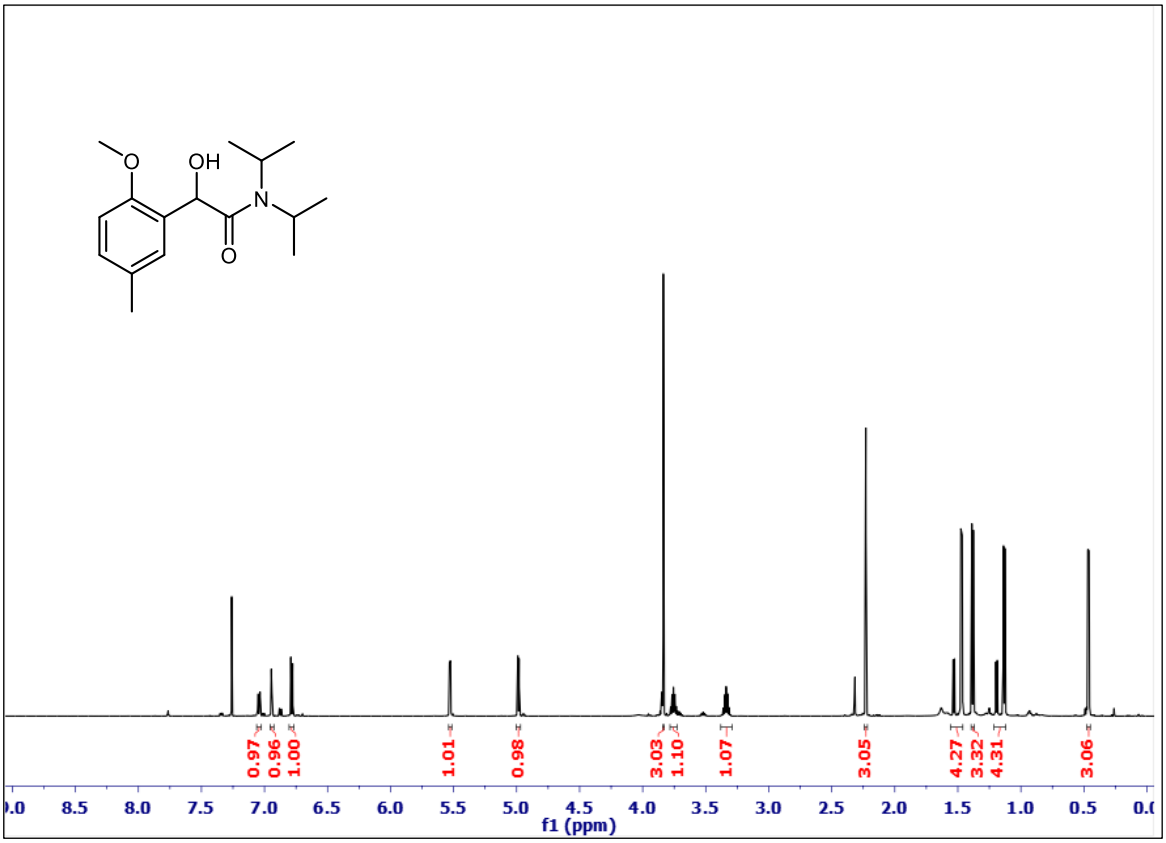


^{13}C NMR (150 MHz, $CDCl_3$)

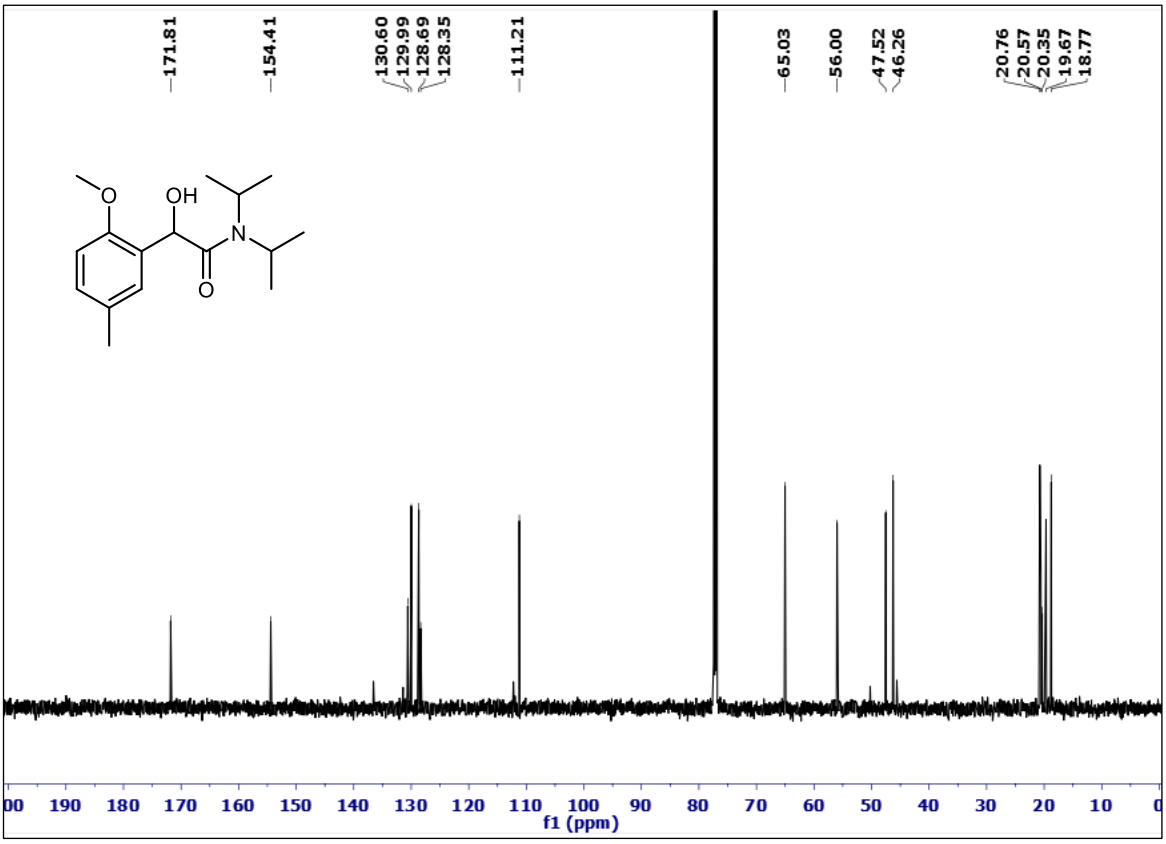


2-Hydroxy-*N*,*N*-diisopropyl-2-(2-methoxy-5-methylphenyl)acetamide (5a)

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



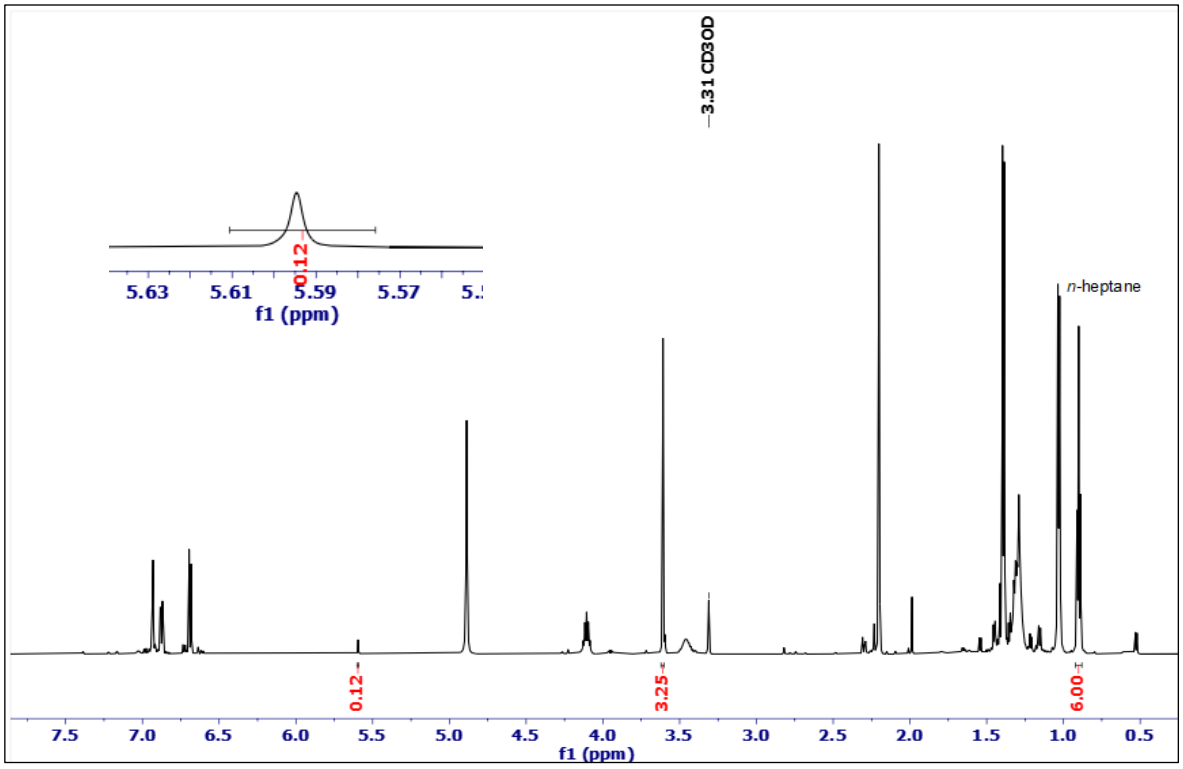


Figure S5: entry 1: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **2a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (1.0 eq., 1 M in 2-MeTHF, 0.20 mL) at RT. Yield **3a**: 6%.

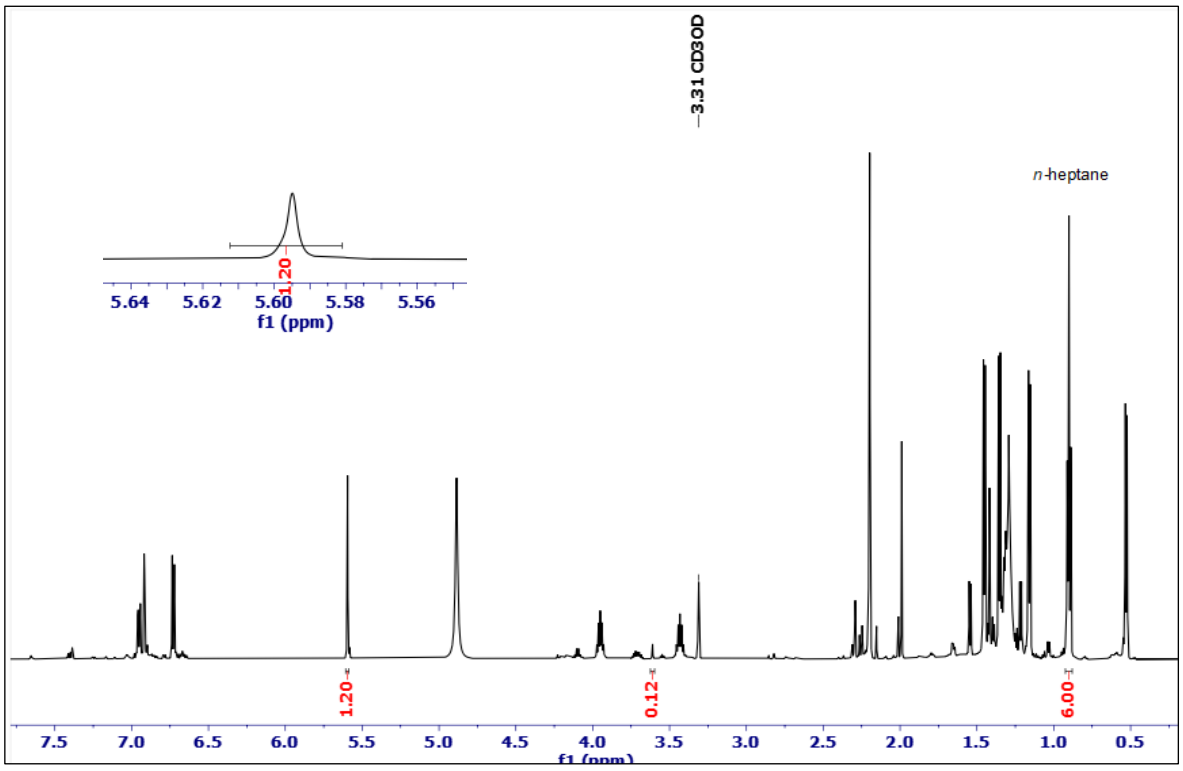


Figure S6: entry 2: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **2a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (2.0 eq., 1 M in 2-MeTHF, 0.40 mL) at RT. Yield **3a**: 60%.

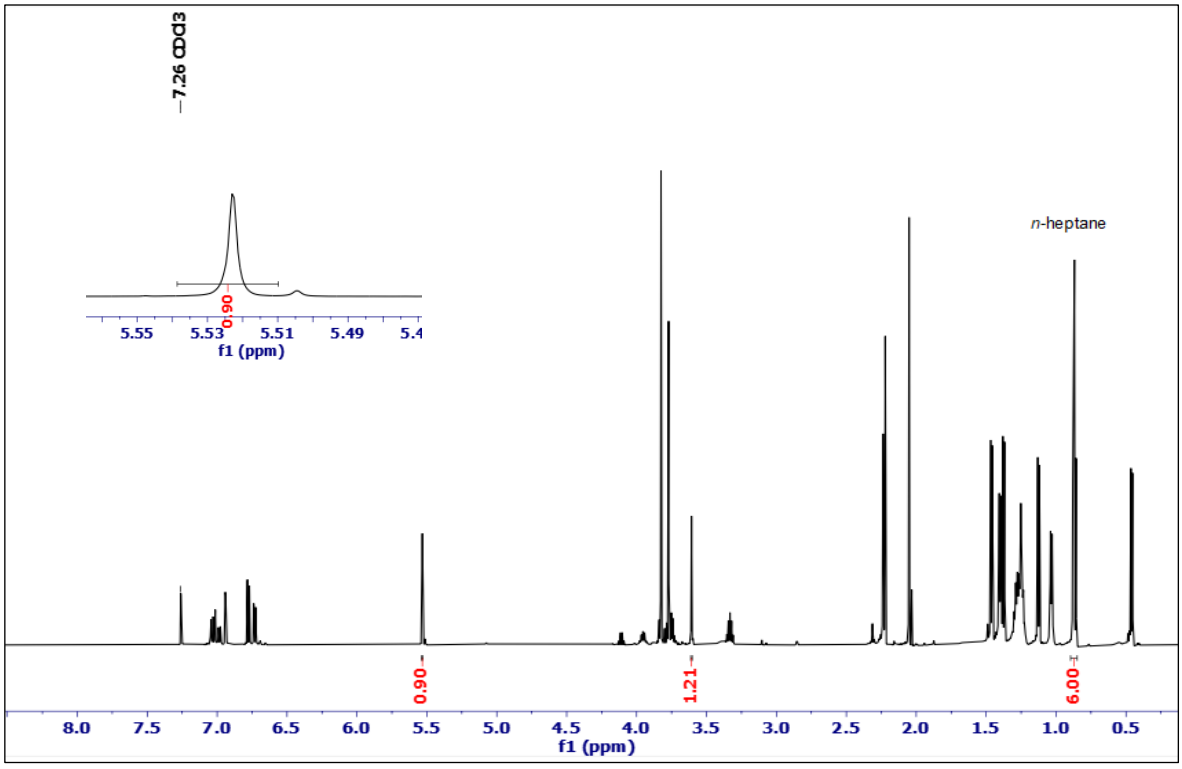


Figure S7: entry 3: crude ^{1}H NMR spectrum in $CDCl_3$ of the reaction performed on **4a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (1.0 eq., 1 M in 2-MeTHF, 0.20 mL) at RT. Yield **5a**: 45%.

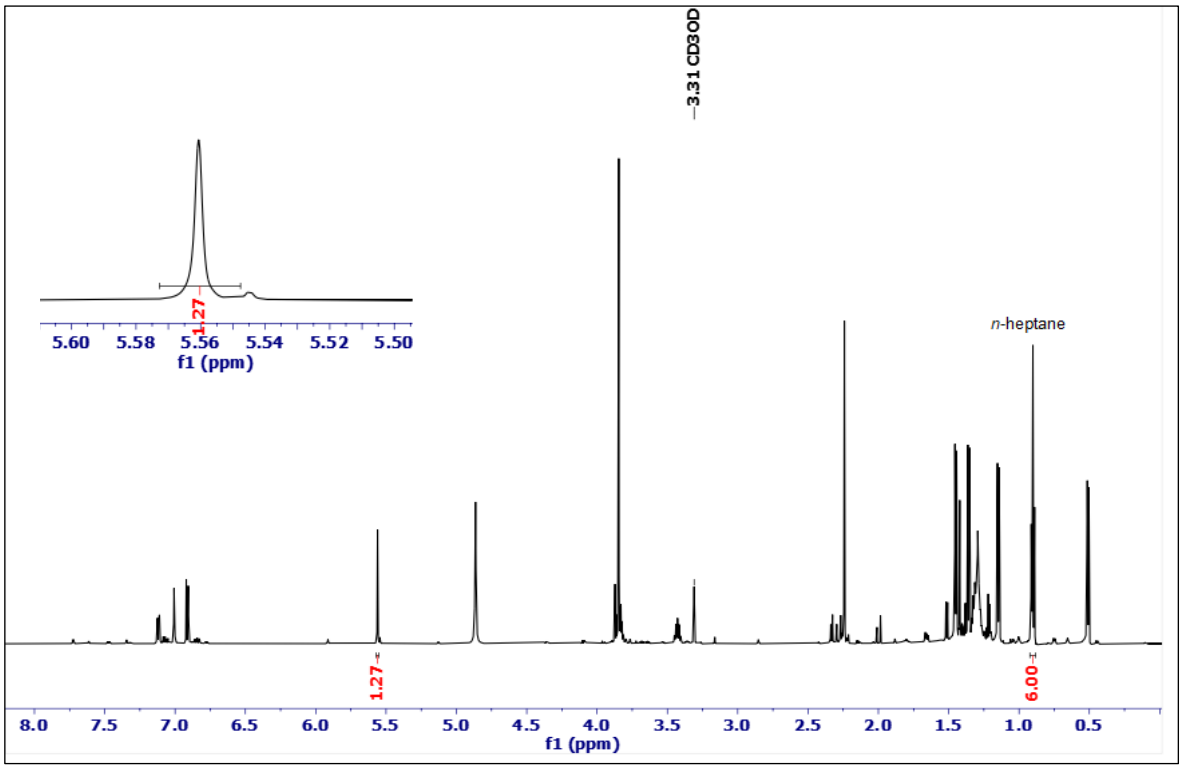
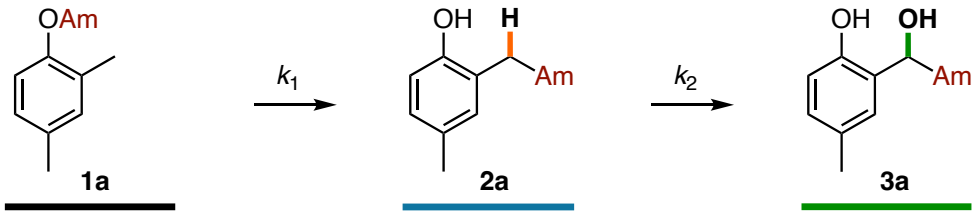


Figure S8: entry 4: crude ^{1}H NMR spectrum in CD_3OD of the reaction performed on **4a** (0.20 mmol), 2-MeTHF (1 mL), LiTMP (2.0 eq., 1 M in 2-MeTHF, 0.40 mL) at RT. Yield **5a**: 63%.

Kinetic analysis of the *homo*-Fries rearrangement/oxidation of carbamate **1a**



In 2-MeTHF. Reactions were performed under air at room temperature. To a stirred solution of **1a** (0.20 mmol, 50 mg) in 2-MeTHF (1 mL), LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) was added. The resulting reaction mixture was stirred for the selected reaction time under air and then quenched with 2 M HCl. The aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated reduced pressure.

In Deep Eutectic Solvent. Reactions were performed under air at room temperature. In an open screw cap vial, **1a** (0.20 mmol, 50 mg) was dissolved in 2-MeTHF (0.20 mL), then ChCl/Gly (1:2 mol mol^{-1}, 1 g) was added and the resulting mixture was vigorously stirred for 5 min to create an emulsion. LiTMP (3.0 eq., 0.60 mmol, 1 M in 2-MeTHF) was rapidly spread over the heterogeneous mixture, which was kept under vigorous stirring and quenched with 1 M HCl after the selected time. The mixture was extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure.

The yields were determined by quantitative ^{1}H NMR using *n*-heptane (0.10 mmol, 14 µL) as the internal standard and a diluting factor 1 for the preparation of the sample (see Eq. 1).

Table S2: kinetic studies on substrate **1a** in 2-MeTHF.

	Replicate 1			Replicate 2			Replicate 3		
Time (s)	**1a [M]**	**2a [M]**	**3a [M]**	**1a [M]**	**2a [M]**	**3a [M]**	**1a [M]**	**2a [M]**	**3a [M]**
0	0.125	0.000	0.000	0.125	0.000	0.000	0.125	0.000	0.000
2	0.038	0.088	0.000	0.011	0.102	0.000	0.015	0.100	0.000
5	0.008	0.117	0.000	0.013	0.112	0.000	0.013	0.112	0.000
15	0.010	0.105	0.005	0.003	0.118	0.000	0.006	0.113	0.000
30	0.000	0.111	0.004	0.000	0.108	0.008	0.000	0.114	0.006
60	0.000	0.113	0.009	0.000	0.110	0.013	0.000	0.111	0.015
120	0.000	0.094	0.018	0.000	0.084	0.013	0.000	0.088	0.011
300	0.000	0.071	0.035	0.000	0.075	0.029	0.000	0.074	0.039
600	0.000	0.038	0.053	0.000	0.050	0.063	0.000	0.030	0.056
900	0.000	0.026	0.063	0.000	0.043	0.046	0.000	0.044	0.046
1800	0.000	0.000	0.080	0.000	0.000	0.079	0.000	0.000	0.075
2700	0.000	0.000	0.075	0.000	0.000	0.066	0.000	0.000	0.071
3600	0.000	0.000	0.075	0.000	0.000	0.063	0.000	0.000	0.059

Table S3: kinetic studies on substrate **1a** in heterogeneous ChCl/Gly (1:2 mol mol^{-1}) / 2-MeTHF solvent mixture.[a]

	Replicate 1		Replicate 3		Replicate 3	
Time (s)	**1a [M]**	**2a [M]**	**1a [M]**	**2a [M]**	**1a [M]**	**2a [M]**
0	0.111	0.000	0.111	0.000	0.111	0.000
1	0.027	0.077	0.019	0.079	0.033	0.077
2	0.022	0.074	0.021	0.074	0.017	0.081
5	0.019	0.076	0.017	0.079	0.017	0.088
10	0.016	0.084	0.014	0.086	0.017	0.090
15	0.020	0.076	0.019	0.089	0.022	0.082
30	0.013	0.081	0.019	0.083	0.013	0.089
1000	0.014	0.081	0.019	0.081	0.013	0.090

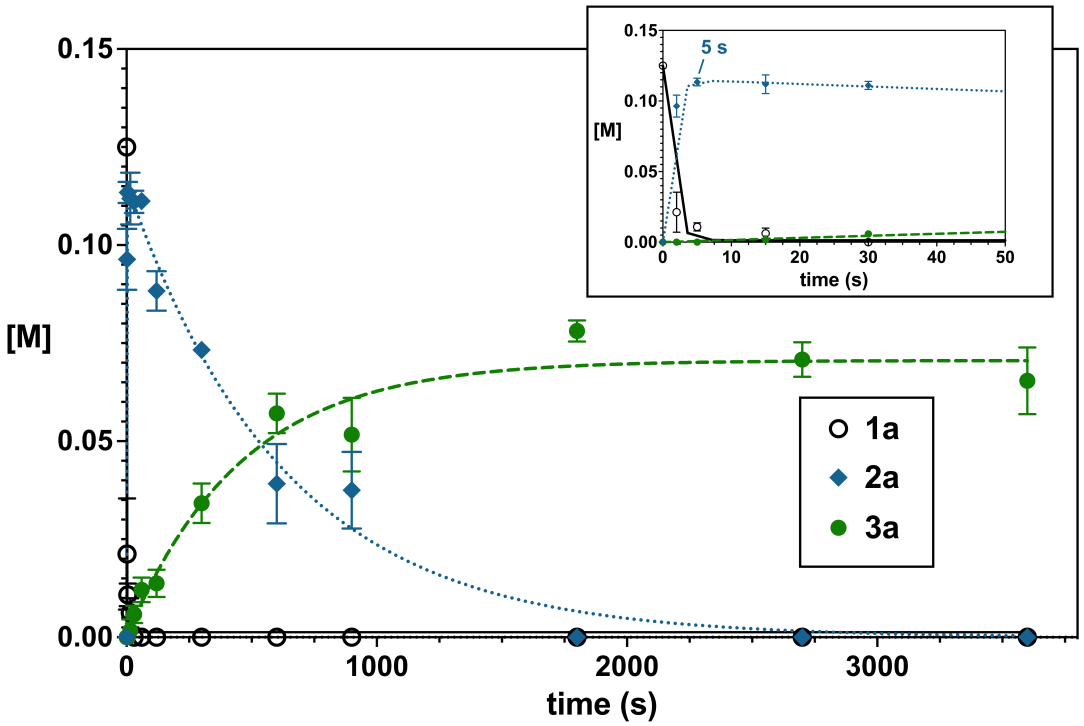


Figure S9: Plots of **1a**, **2a** and **3a** concentrations [M] versus time (s) for the metalation of carbamate **1a** (0.20 mmol) with LiTMP (0.60 mmol, 1 M in 2-MeTHF) at 25 °C, under air. The curves represent unweighted least-squares fits. 2-MeTHF (0.125 M) was used as solvent. k_1 = 1.1 ± 0.1 s^{-1}; k_2 = (1.9 ± 0.5) × 10^{-3} s^{-1}. Inset: expansion of the reaction profile after 50 s.

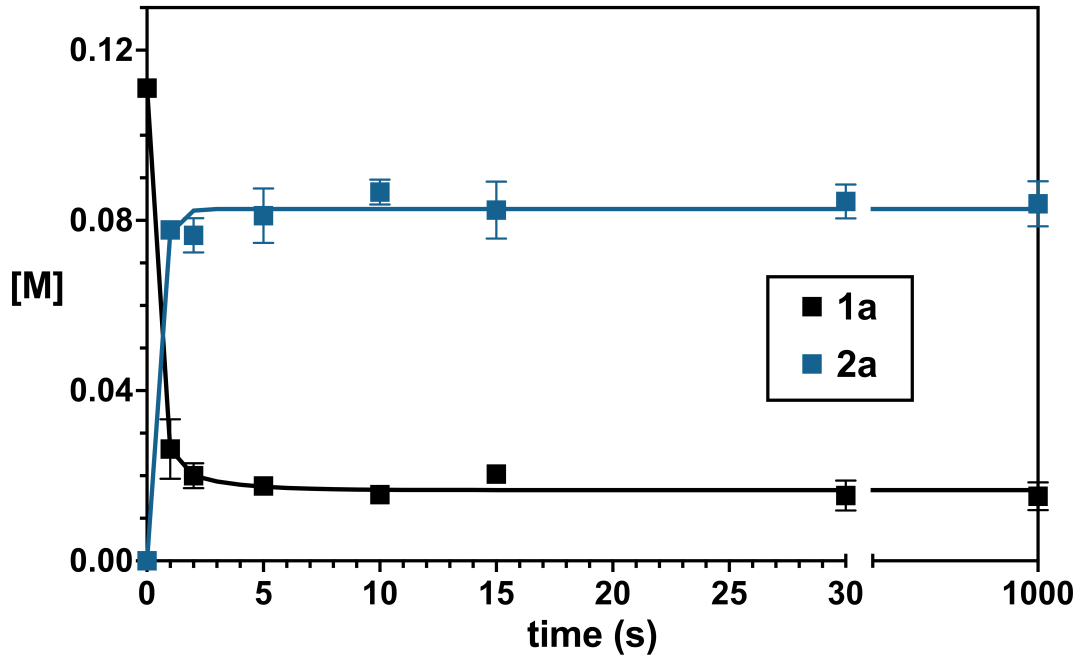
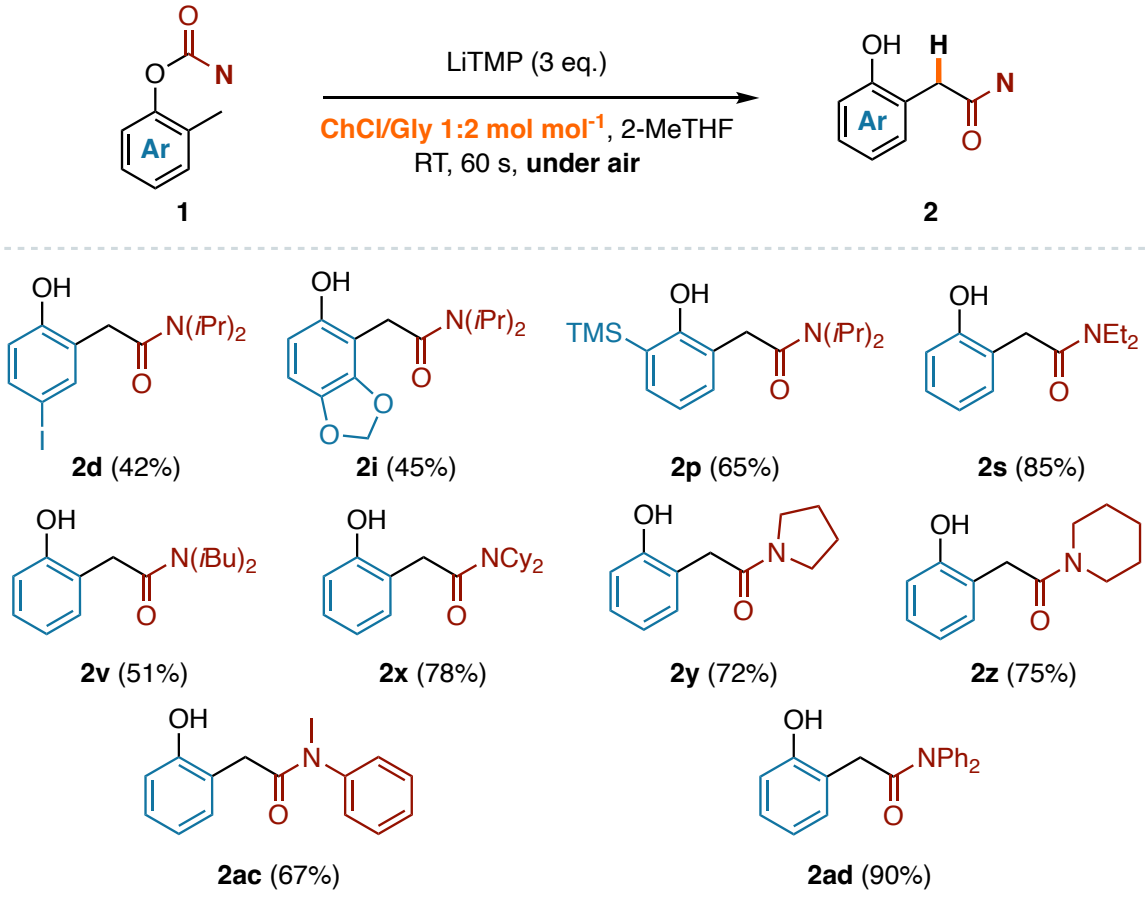


Figure S10: Plots of **1a** and **2a** concentrations [M] versus time (s) for the metalation of carbamate **1a** (0.20 mmol) with LiTMP (1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) at 25 °C, under air. The curves represent unweighted least-squares fits. ChCl/Gly 1:2 mol mol^{-1}/2-MeTHF heterogeneous mixture (0.111 M) was used as solvent. k_1 = 3.0 ± 0.8 s^{-1}.

Homo-Fries rearrangement of carbamates **1** in Deep Eutectic Solvents

General procedure. Reactions were performed under air at room temperature. In an open screw cap vial, the appropriate carbamate **1** (0.20 mmol, 1 eq.) was dissolved in 2-MeTHF (0.20 mL, 1 M), then ChCl/Gly (1:2 mol mol^{-1}) (1 g) was added and the resulting mixture was vigorously stirred for 5 min to create an emulsion. LiTMP (3.0 eq., 1 M in 2-MeTHF, 0.60 mmol, 0.6 mL) was rapidly spread over the heterogeneous mixture, which was kept under vigorous stirring and quenched with 1 M HCl after 1 min. The mixture was extracted with EtOAc (3 x 10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography.[4]



2-(2-Hydroxy-5-iodophenyl)-*N,N*-diisopropylacetamide (2d): General procedure starting from **1d** (72 mg). Purification by flash column chromatography (petroleum ether/Et_2O 8/2 v/v) gave **2d** as a white solid (30 mg, 42%, R_f = 0.25 petroleum ether/Et_2O 8/2 v/v), mp. 158.0-159.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.42 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 4.17 (quint, *J* = 6.8 Hz, 1H), 3.75-3.51 (m, 3H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.27 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 157.6, 138.5, 137.7, 124.3, 120.7, 81.2, 60.0, 50.2, 46.9, 38.4, 30.5, 21.4, 20.5. HRMS (ESI): *m/z* calcd for $C_{14}H_{20}INO_2 + H^+$: 362.0611 [M+H$^+$]; found 362.0611.

2-(5-Hydroxybenzo[d][1,3]dioxol-4-yl)-*N,N*-diisopropylacetamide (2i): General procedure starting from **1i** (56 mg). Purification by flash column chromatography (petroleum ether/EtOAc 9/1 v/v) gave **2i** as a white solid (25 mg, 45%, R_f = 0.28 petroleum ether/EtOAc 9/1 v/v), mp. 172.0-173.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 5.88 (s, 2H), 4.39-4.24 (m, 1H), 3.70 (s, 2H) superimposed to 3.66-3.50 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 152.6, 145.5, 140.1, 109.1, 107.6, 105.4, 101.0, 46.7, 31.6, 21.1, 20.5. HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NO_4 + H^+$: 280.1543 [M+H$^+$]; found 280.1543.

2-(2-Hydroxy-6-(trimethylsilyl)phenyl)-*N,N*-diisopropylacetamide (2p): General procedure starting from **1p** (62 mg). Purification by flash column chromatography (petroleum ether/Et_2O 99/1 v/v) gave **2p** as a colourless oil (40 mg, 65%, R_f = 0.20 petroleum ether/ Et_2O 99/1 v/v), mp. 102.0-103.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.76-7.71 (m, 1H), 7.47 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 4.75-4-61 (m, 1H), 4.14 (s, 2H) superimposed to 4.16-3.98 (m, 1H), 1.78 (d, *J* = 6.7 Hz, 6H), 1.70 (d, *J* = 6.8 Hz, 6H), 0.75 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 162.5, 134.4, 131.7, 128.2, 120.6, 119.5, 46.7, 39.2, 21.4, 20.5, -0.8. HRMS (ESI): *m/z* calcd for $C_{17}H_{29}NO_2Si + H^+$: 308.2040 [M+H$^+$]; found 308.2040.

2-(2-Hydroxyphenyl)-*N,N*-diethylacetamide (2s): General procedure starting from **1s** (41 mg). Purification by flash column chromatography (petroleum ether/EtOAc 9/1 v/v) gave **2s** as a yellow oil (35 mg, 85%, R_f = 0.10 petroleum ether/EtOAc 9/1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H) superimposed to 6.98 (d, *J* = 8.1 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 3.71 (s, 2H), 3.50 (q, *J* = 7.4 Hz, 2H), 3.39 (q, *J* = 7.06 Hz, 2H), 1.29 (t, *J* = 7.3 Hz, 3H), 1.13 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 157.5, 130.5, 129.1, 121.3, 120.0, 118.4, 43.7, 41.5, 37.1, 14.9, 13.0.[12]

2-(2-Hydroxyphenyl)-*N,N*-diisobutylacetamide (2v): General procedure starting from **1v** (53 mg). Purification by flash column chromatography (petroleum ether/EtOAc 98/2 v/v) gave **2v** as a white solid (27 mg, 51%, R_f = 0.21 petroleum ether/EtOAc 98/2 v/v), mp. 75.0-76.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.03-6.93 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 3.73 (s, 2H), 3.27 (d, *J* = 7.6 Hz, 2H), 3.22 (d, *J* = 7.6 Hz, 2H), 2.10-1.91 (m, 2H), 0.98 (d, *J* = 6.7 Hz, 6H), 0.81 (d, *J* = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.0, 157.4, 130.5, 129.1, 121.4, 119.9, 118.4, 57.0, 54.4, 37.4, 28.8, 26.7, 20.3, 20.1. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NO_2 + H^+$: 264.1958 [M+H$^+$]; found 264.1958.

2-(2-Hydroxyphenyl)-*N,N*-dicyclohexylacetamide (2x): General procedure starting from **1x** (63 mg). Purification by flash column chromatography (petroleum ether/Et_2O 8/2 v/v) gave **2x** as a white solid (49 mg, 78%, R_f = 0.23 petroleum ether/Et_2O 8/2 v/v), mp. 189.0-190.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H) superimposed to 6.96 (d, *J* = 8.1 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 3.90-3.63 (m, 3H), 2.94 (br s, 1H) 2.41 (br s, 2H), 1.87 (d, *J* = 13.2 Hz, 2H), 1.80-1.29 (m, 14H), 1.28-1.07 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.34, 129.95, 128.73, 121.34, 119.79, 118.01, 65.86, 59.79, 56.77, 39.31, 31.20, 29.85, 26.41, 26.00, 25.26, 25.17, 15.28. HRMS (ESI): *m/z* calcd for $C_{20}H_{29}NO_2 + H^+$: 316.2271 [M+H$^+$]; found 316.2271.

2-(2-Hydroxyphenyl)-1-(pyrrolidin-1-yl)ethan-1-one (2y): General procedure starting from **1y** (41 mg). Purification by flash column chromatography (petroleum ether/EtOAc 9/1 v/v) gave **2y** as a white solid (30 mg, 72%, R_f = 0.05 petroleum ether/EtOAc 9/1 v/v), mp. 115.0-116.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.81 (td, *J* = 7.4, 1.3 Hz, 1H), 3.71-3.62 (m, 4H), 3.46 (t, *J* = 6.9 Hz, 2H), 2.00 (quint, *J* = 6.8 Hz, 2H), 1.88 (quint, *J* = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.6, 157.4, 130.6, 129.1, 121.1, 120.0, 118.4, 47.7, 46.3, 39.00, 26.1, 24.5.[13]

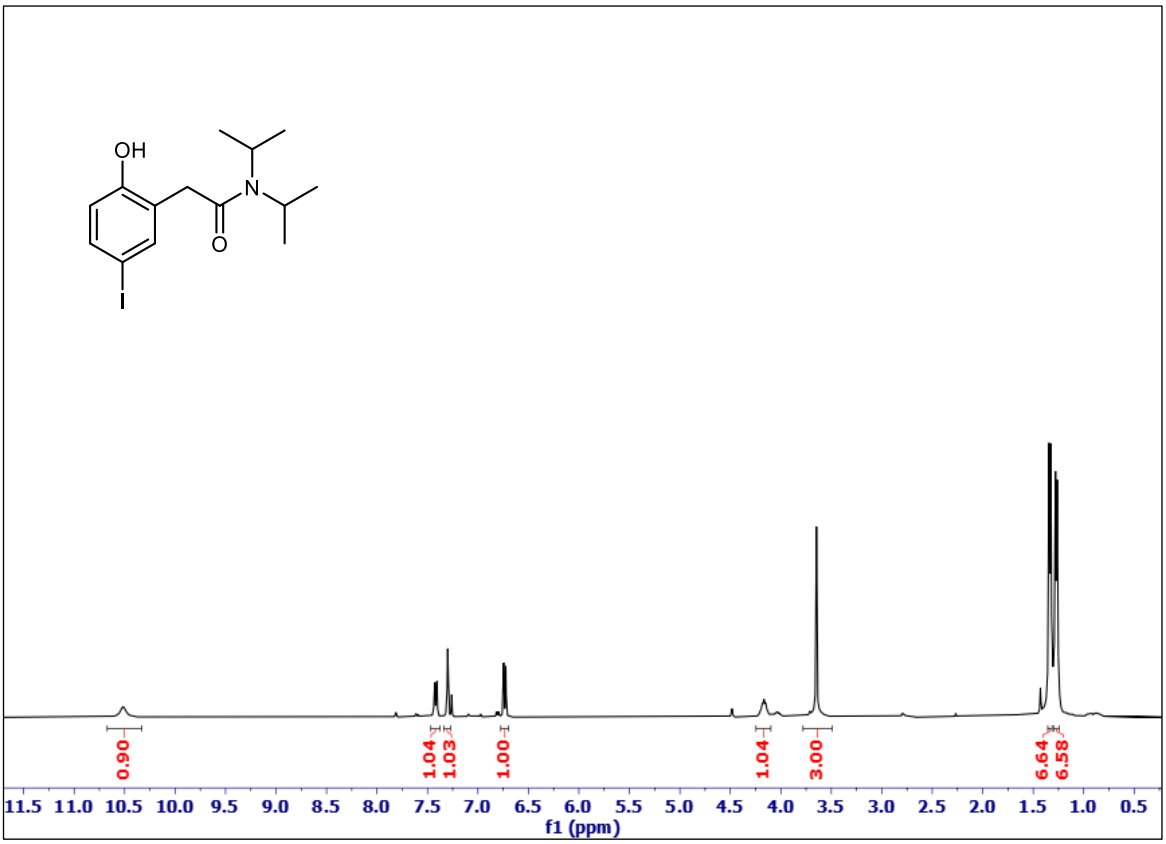
2-(2-Hydroxyphenyl)-1-(piperidin-1-yl)ethan-1-one (2z): General procedure starting from **1z** (44 mg). Purification by flash column chromatography (petroleum ether/EtOAc 9/1 v/v) gave **2z** as a white solid (33mg, 75%, R_f = 0.25 petroleum ether/EtOAc 9/1 v/v), mp. 97.0-98.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.16 (t, *J* = 6.9, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 3.74 (s, 2H), 3.62 (t, *J* = 5.3 Hz, 2H), 3.56 (t, *J* = 5.5 Hz, 2H), 1.70-1.48 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 157.2, 130.2, 129.0, 121.1, 120.1, 118.2, 48.2, 43.5, 36.5, 26.6, 25.4, 24.3.[13]

2-(2-Hydroxyphenyl)-*N*-methyl-*N*-phenylacetamide (2ac): General procedure starting from **1ac** (48 mg). Purification by flash column chromatography (petroleum ether/EtOAc 9/1 v/v) gave **2ac** as a yellow oil (32 mg, 67%, R_f = 0.18 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.57-7.42 (m, 3H), 7.24 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.73 (td, *J* = 7.4, 1.3 Hz, 1H), 6.51 (dd, *J* = 7.5, 1.7 Hz, 1H), 3.48 (s, 2H), 3.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.6, 157., 143.4, 130.5, 130.1, 129.1, 128.8, 127.4, 121.2, 120.0, 118.3, 37.9, 37.6. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}NO_2$ + H^+: 242.1176 [M+H^+]; found 242.1174.

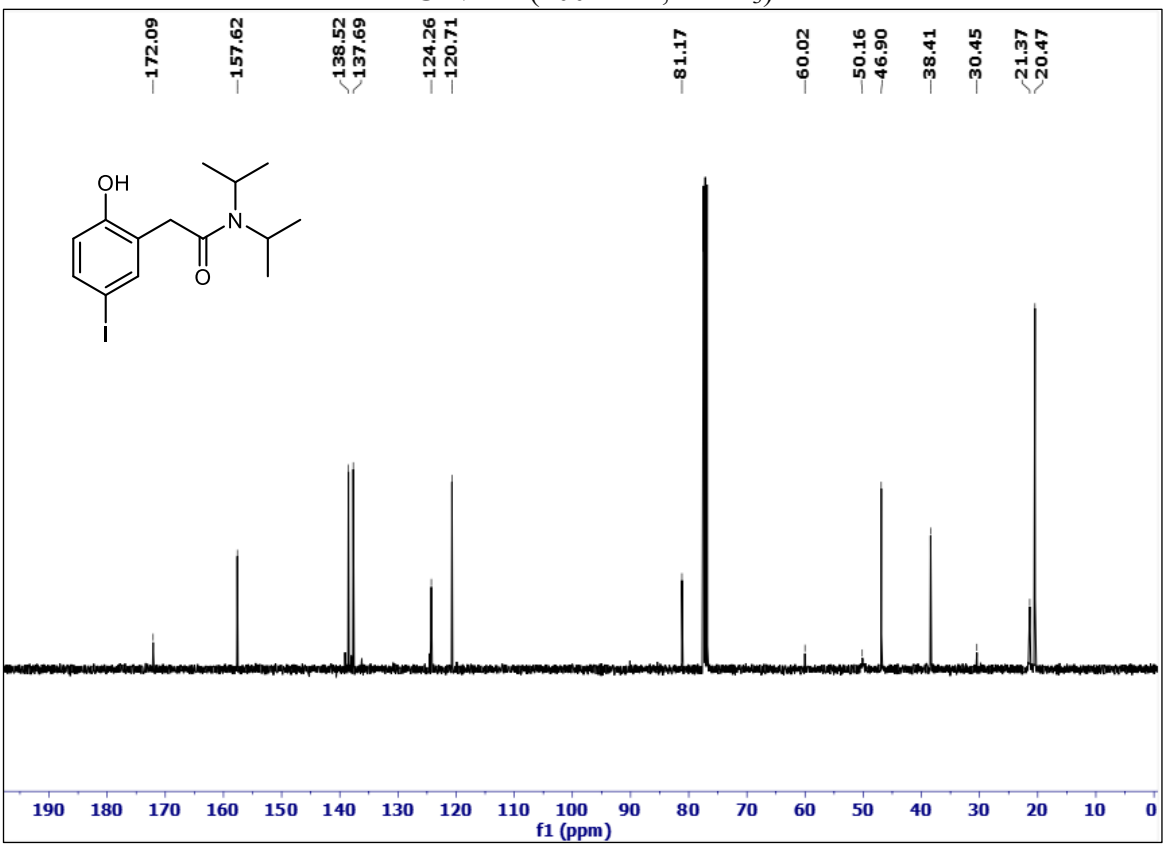
2-(2-Hydroxyphenyl)-*N,N*-diphenylacetamide (2ad): General procedure starting from **1ad** (61 mg). Purification by flash column chromatography (petroleum ether/EtOAc 9/1 v/v) gave **2ad** as a white solid (55 mg, 90%, R_f = 0.23 v/v), mp. 135.0-136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.56-7.43 (m, 3H), 7.40-7.30 (m, 4H), 7.28-7.15 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 3.68 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.9, 157.2, 142.5, 141.8, 130.7, 130.1, 129.5, 129.4, 129.2, 129.1, 128.8, 128.7, 127.4, 127.2, 126.5, 121.0, 120.1, 118.4, 117.9, 38.7. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}NO_2$ + H^+: 304.1332 [M+H^+]; found 304.1332.

2-(2-Hydroxy-5-iodophenyl)-*N*,*N*-diisopropylacetamide (2d)

^{1}H NMR (400 MHz, $CDCl_3$)

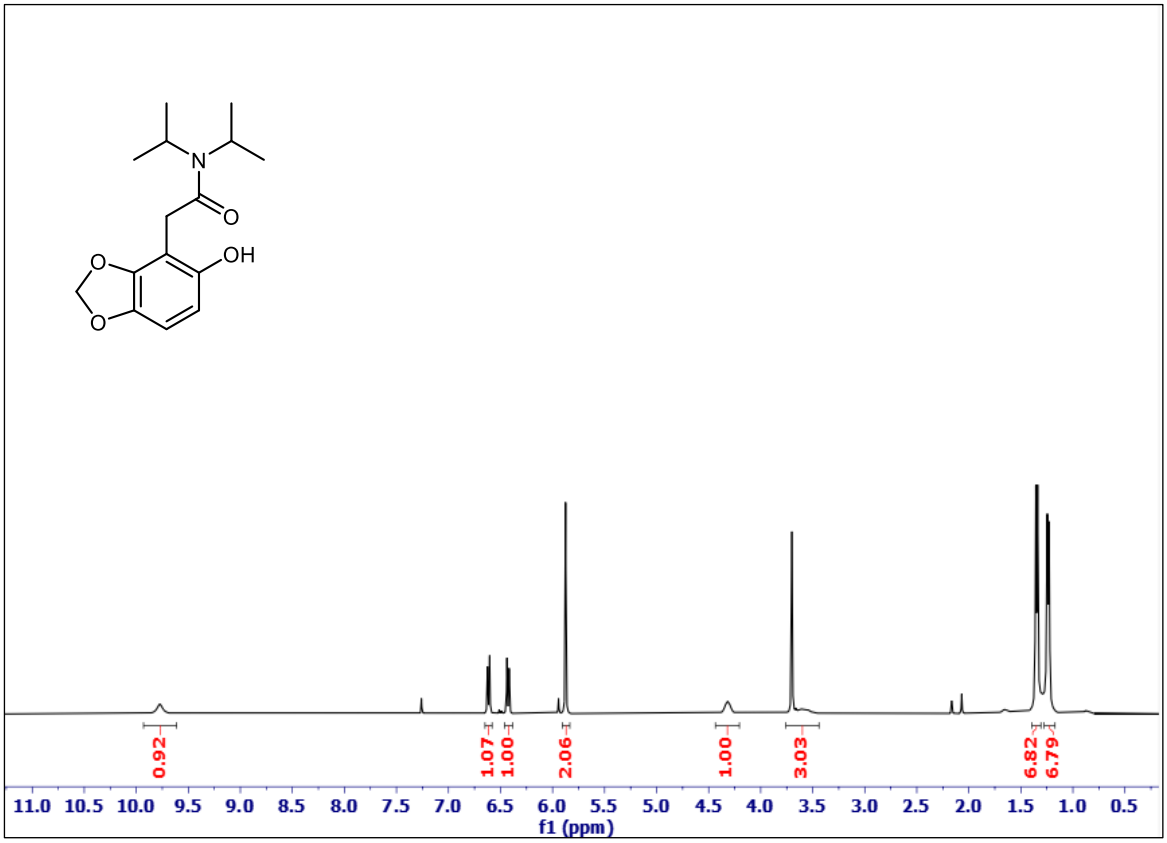


^{13}C NMR (100 MHz, $CDCl_3$)

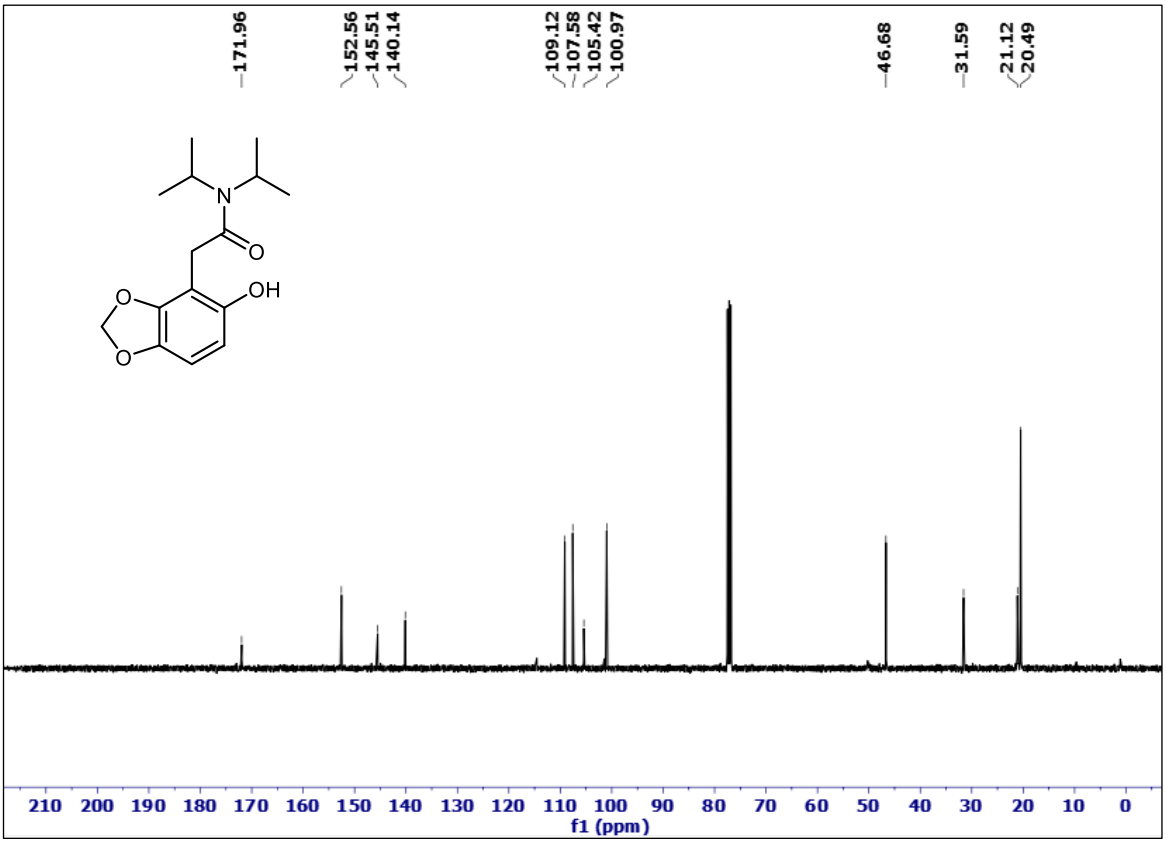


2-(5-Hydroxybenzo[d][1,3]dioxol-4-yl)-*N,N*-diisopropylacetamide (2i)

^{1}H NMR (400 MHz, $CDCl_3$)

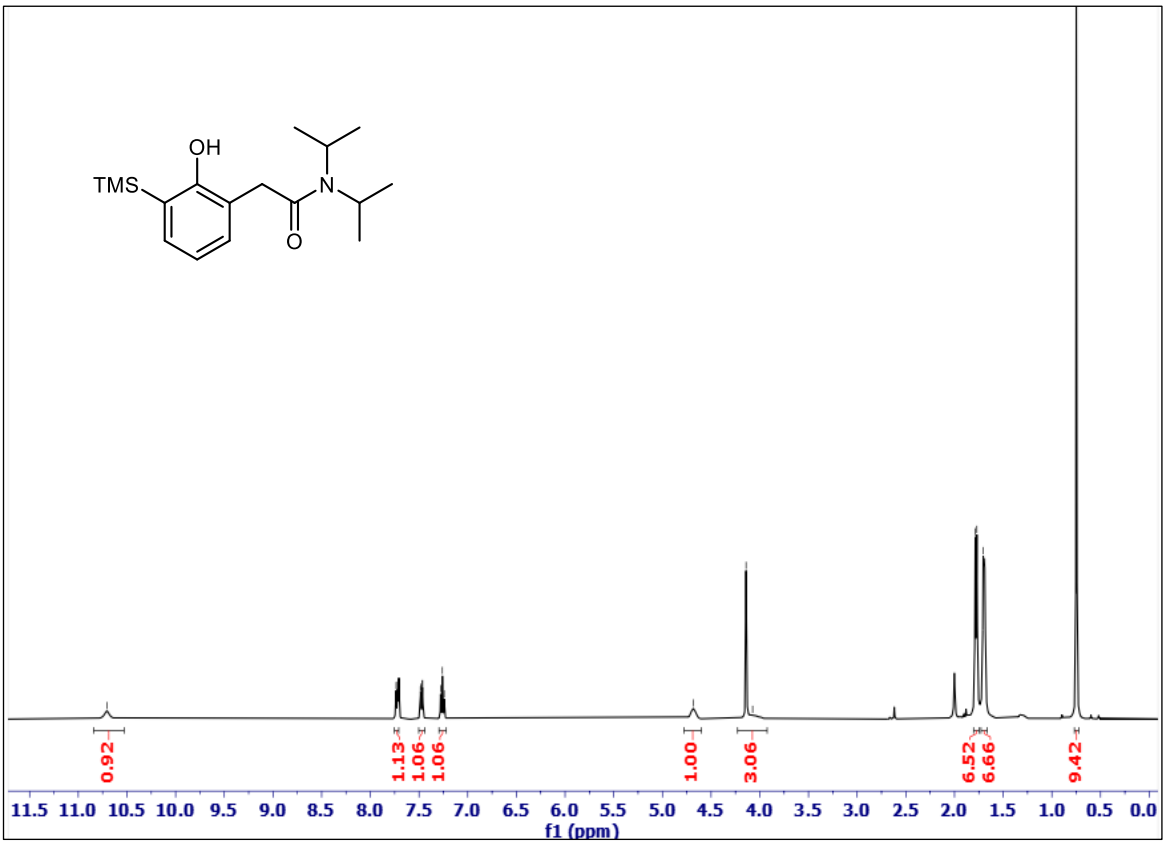


^{13}C NMR (100 MHz, $CDCl_3$)

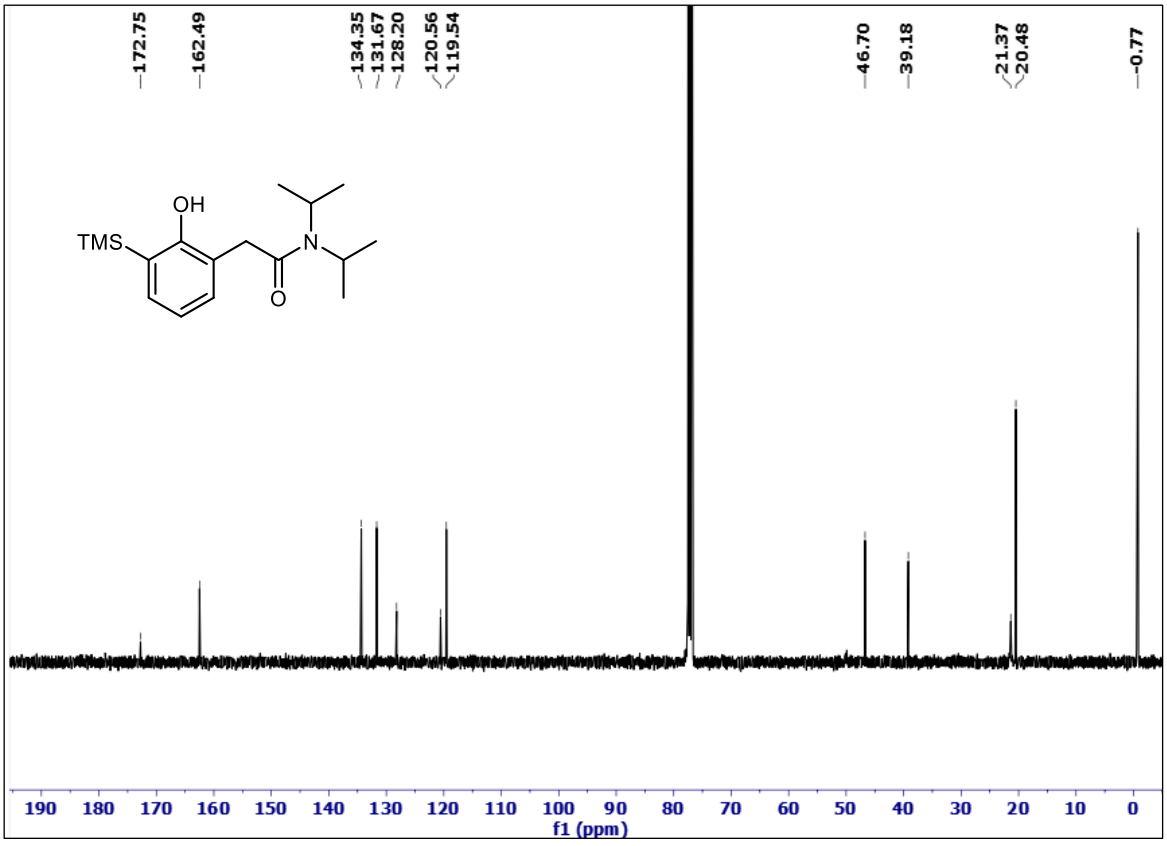


2-(2-Hydroxy-6-(trimethylsilyl)phenyl)-*N,N*-diisopropylacetamide (2p)

^{1}H NMR (400 MHz, $CDCl_3$)

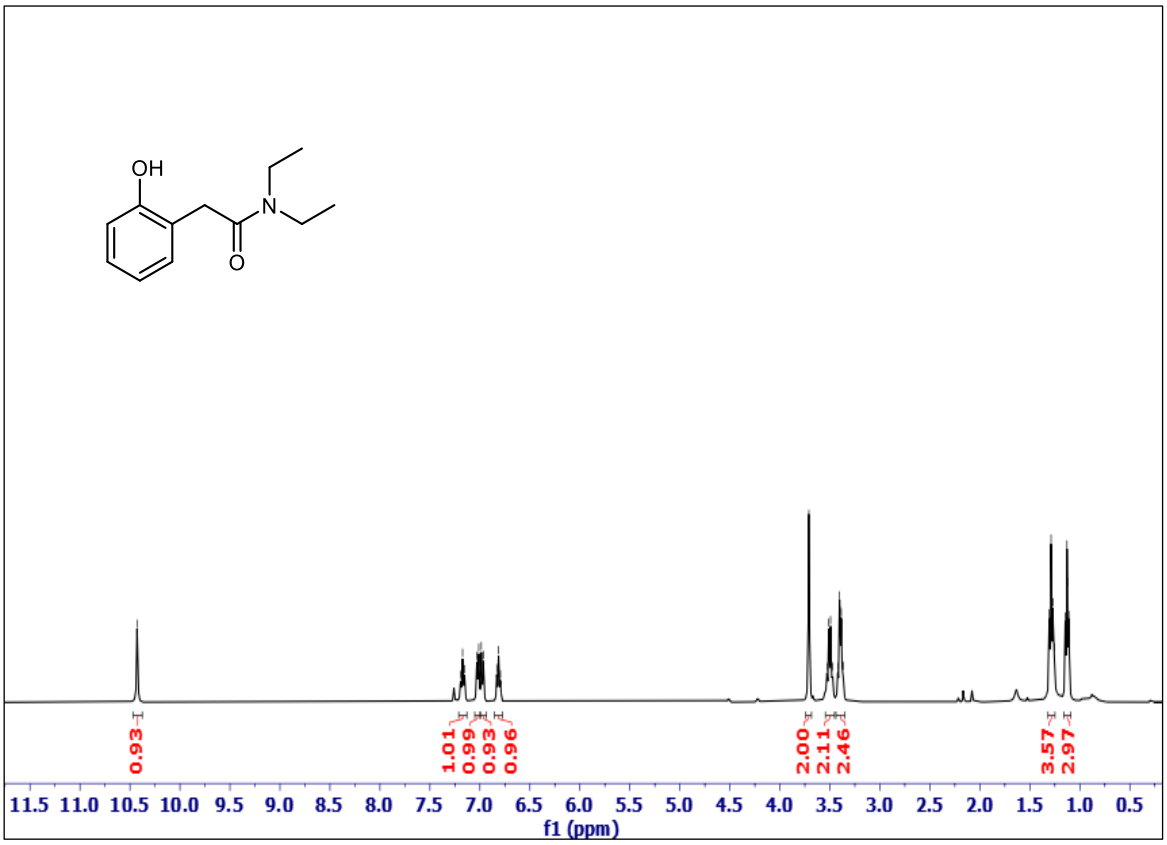


^{13}C NMR (100 MHz, $CDCl_3$)

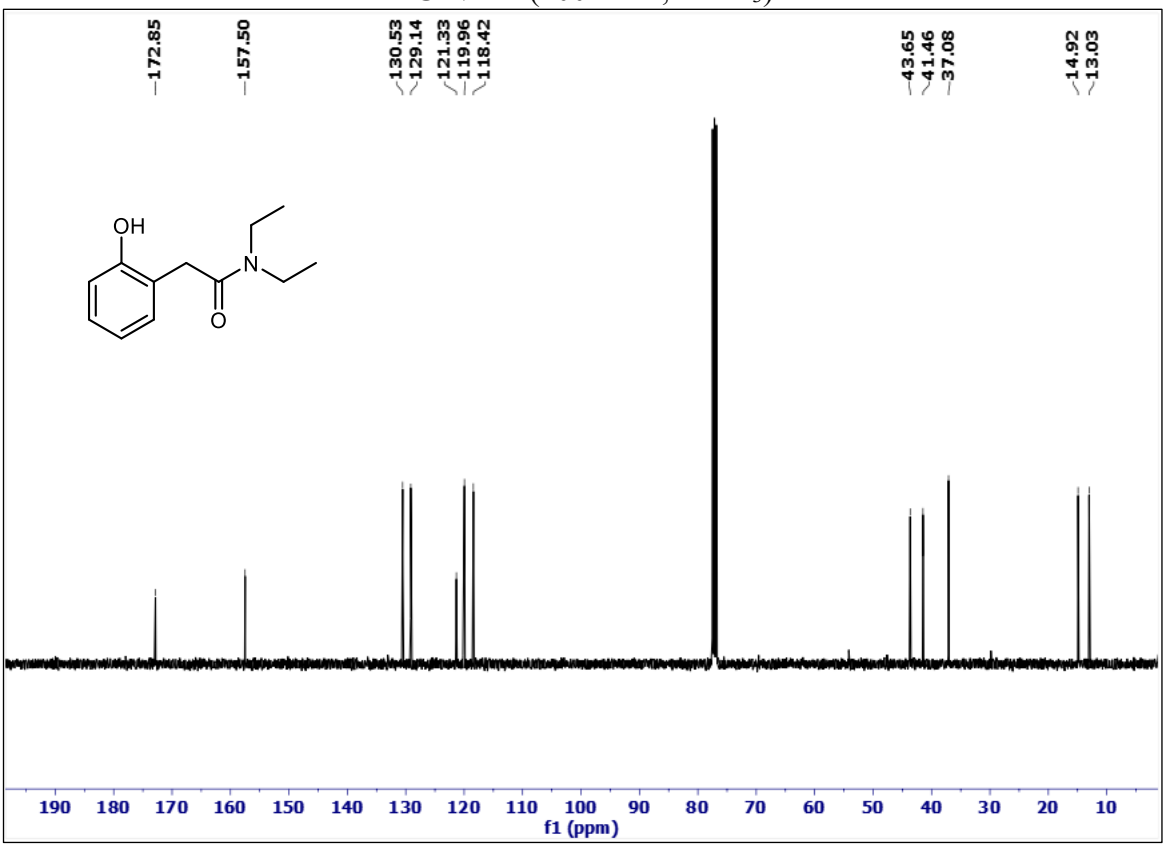


2-(2-Hydroxyphenyl)-*N*,*N*-diisobutylacetamide (2s)

^{1}H NMR (400 MHz, $CDCl_3$)

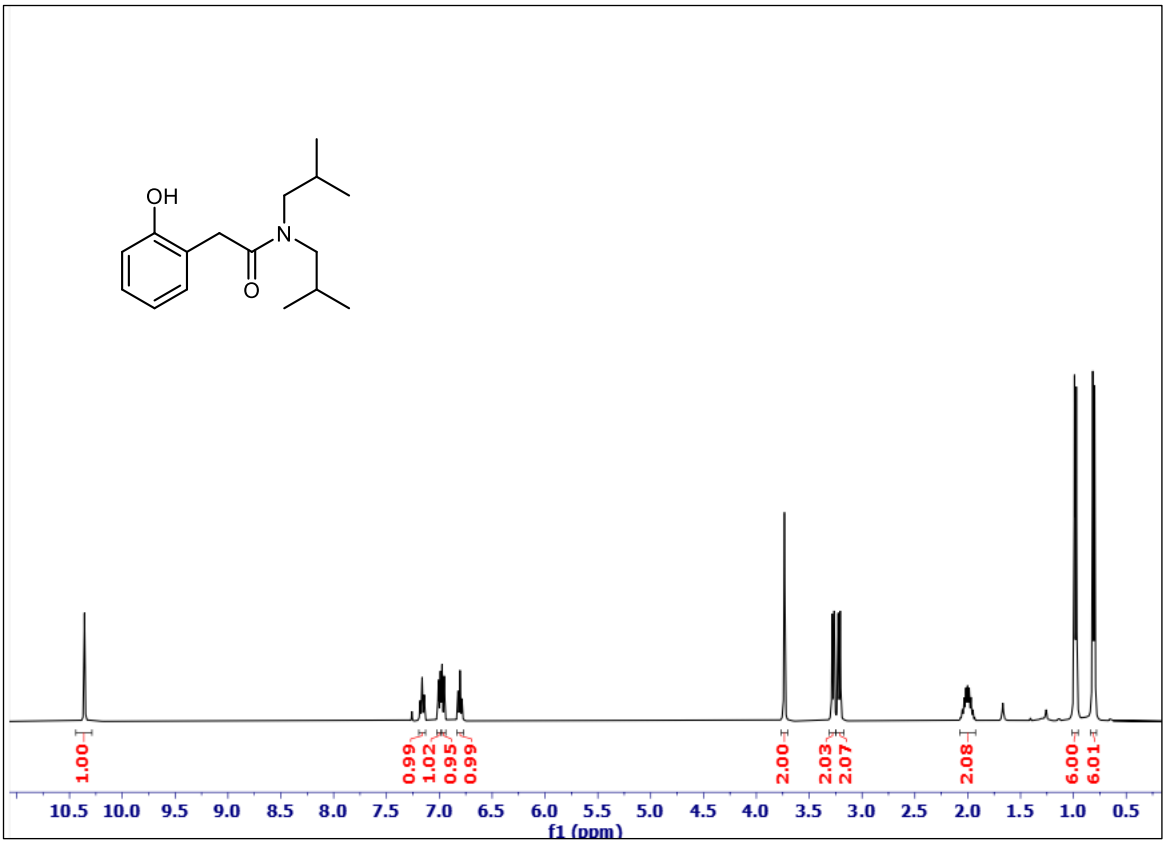


^{13}C NMR (100 MHz, $CDCl_3$)

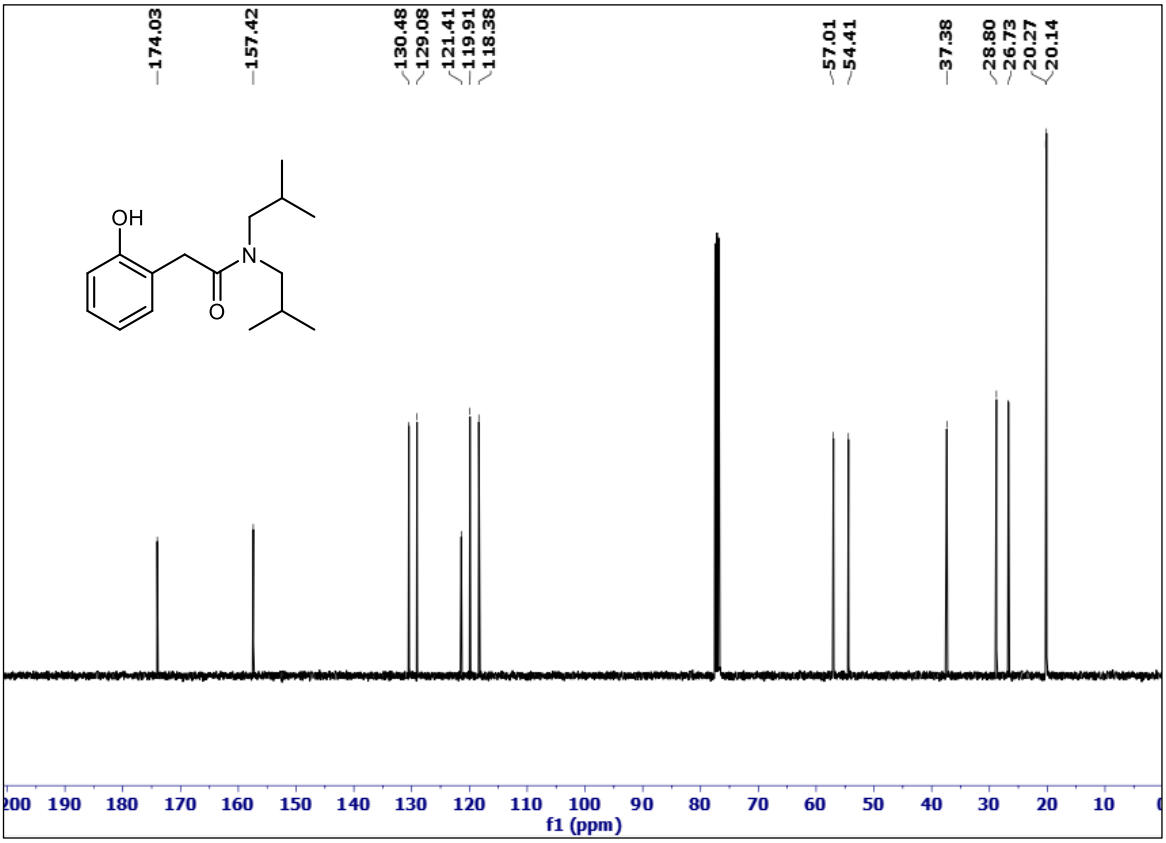


2-(2-Hydroxyphenyl)-*N*,*N*-diisobutylacetamide (2v)

^{1}H NMR (400 MHz, $CDCl_3$)

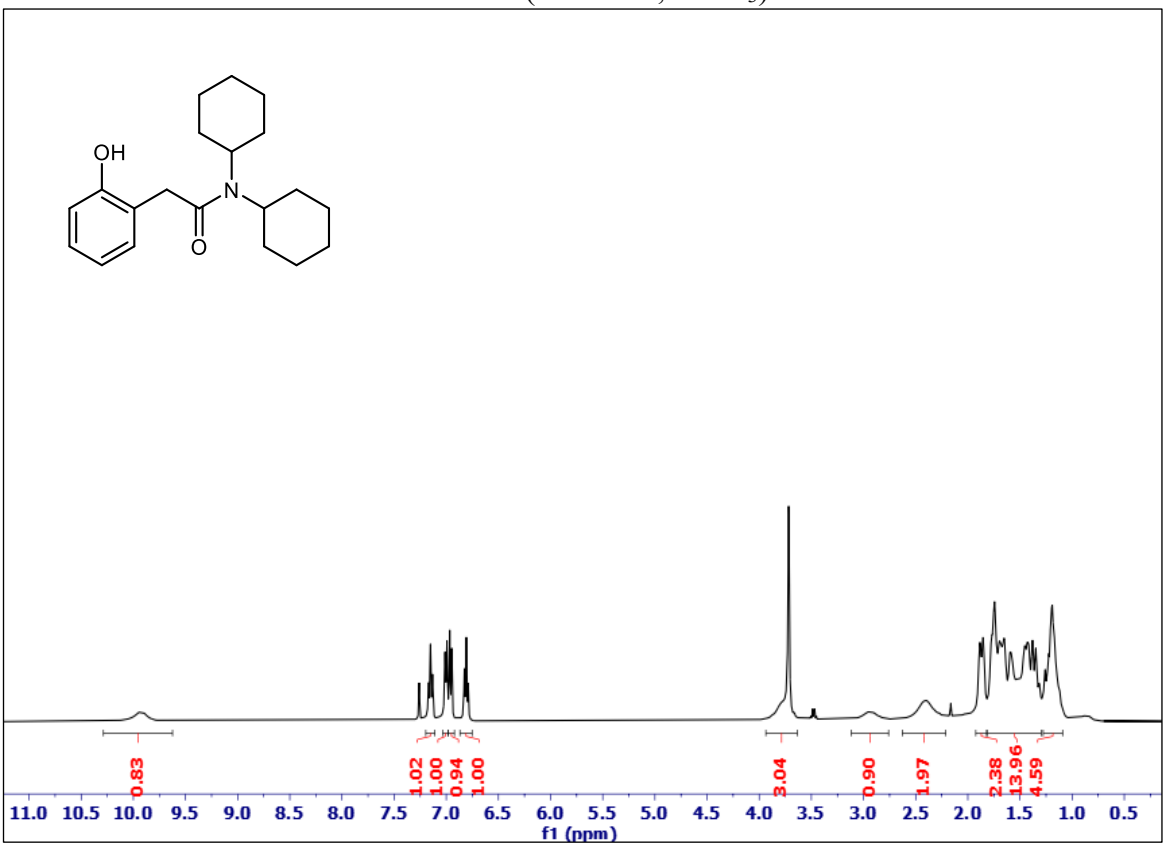


^{13}C NMR (100 MHz, $CDCl_3$)

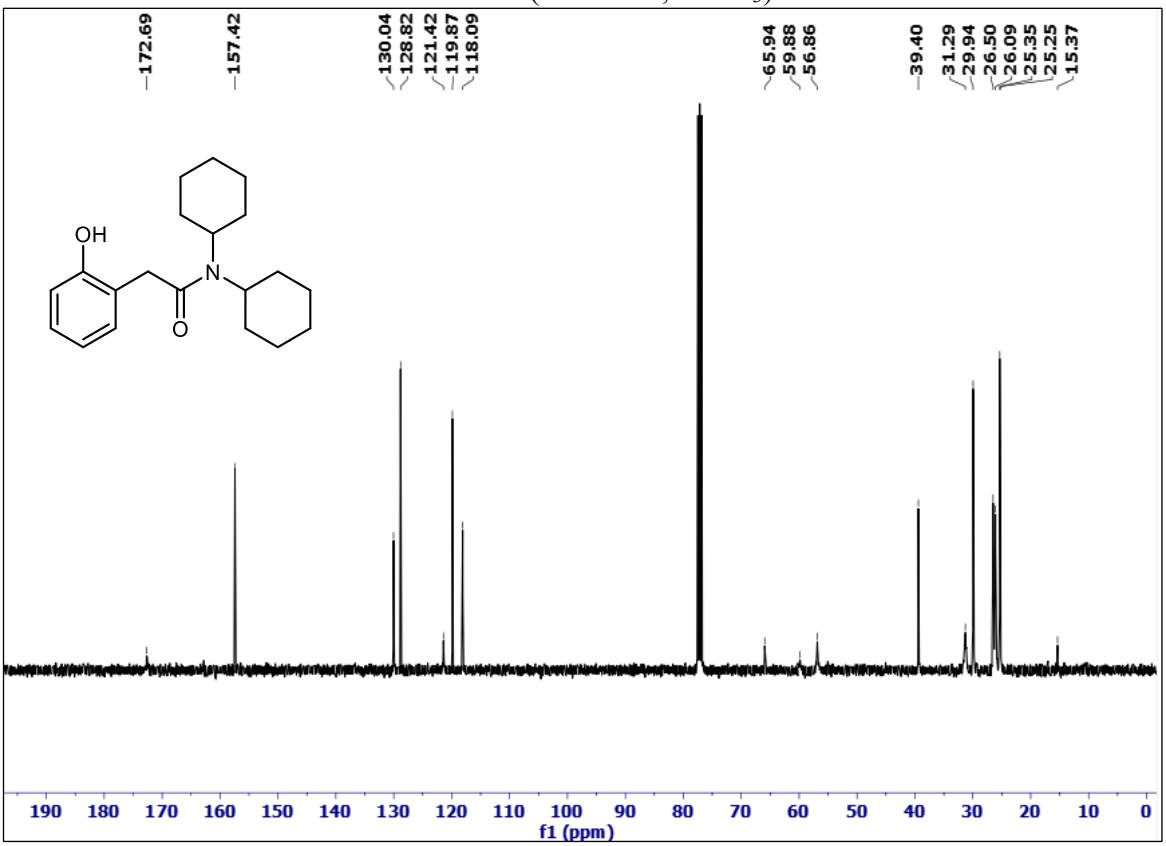


2-(2-Hydroxyphenyl)-*N*,*N*-dicyclohexyl acetamide (2x)

^{1}H NMR (400 MHz, $CDCl_3$)

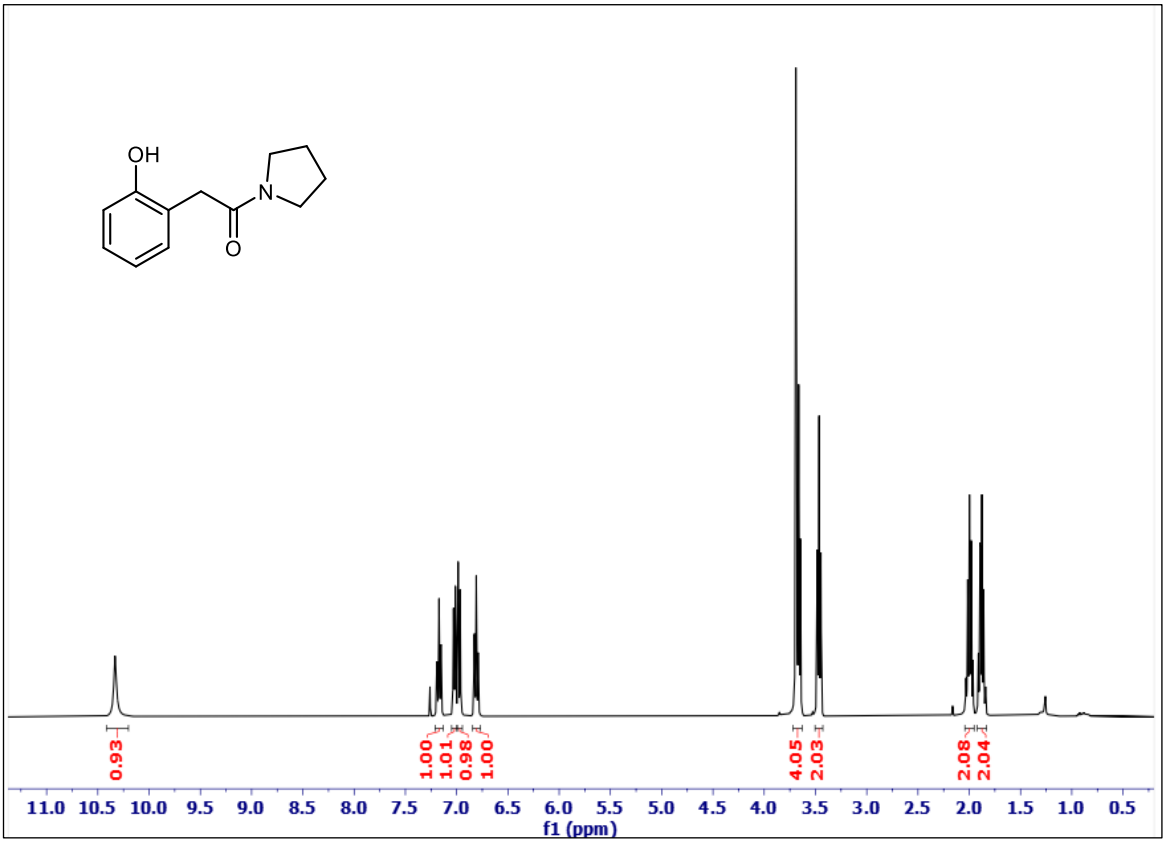


^{13}C NMR (100 MHz, $CDCl_3$)

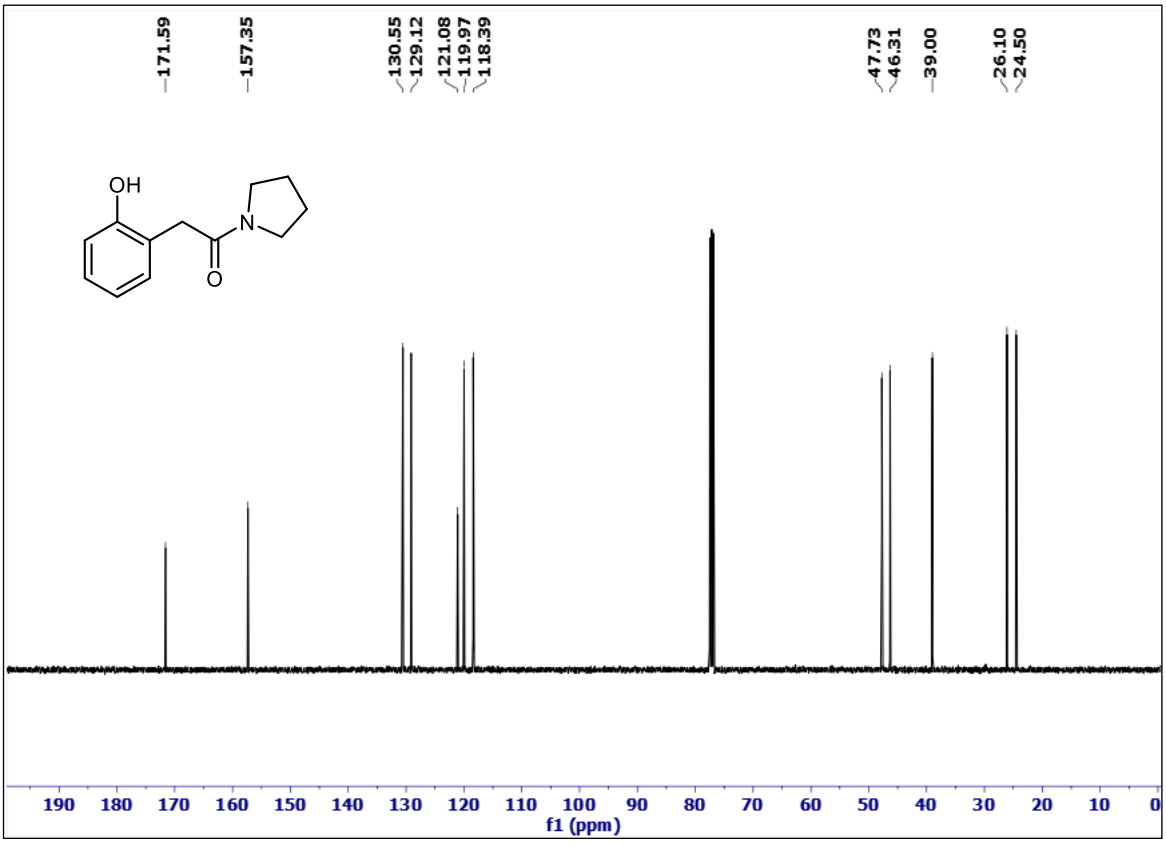


2-(2-Hydroxyphenyl)-1-(pyrrolidin-1-yl)ethan-1-one (2y)

^{1}H NMR (400 MHz, $CDCl_3$)

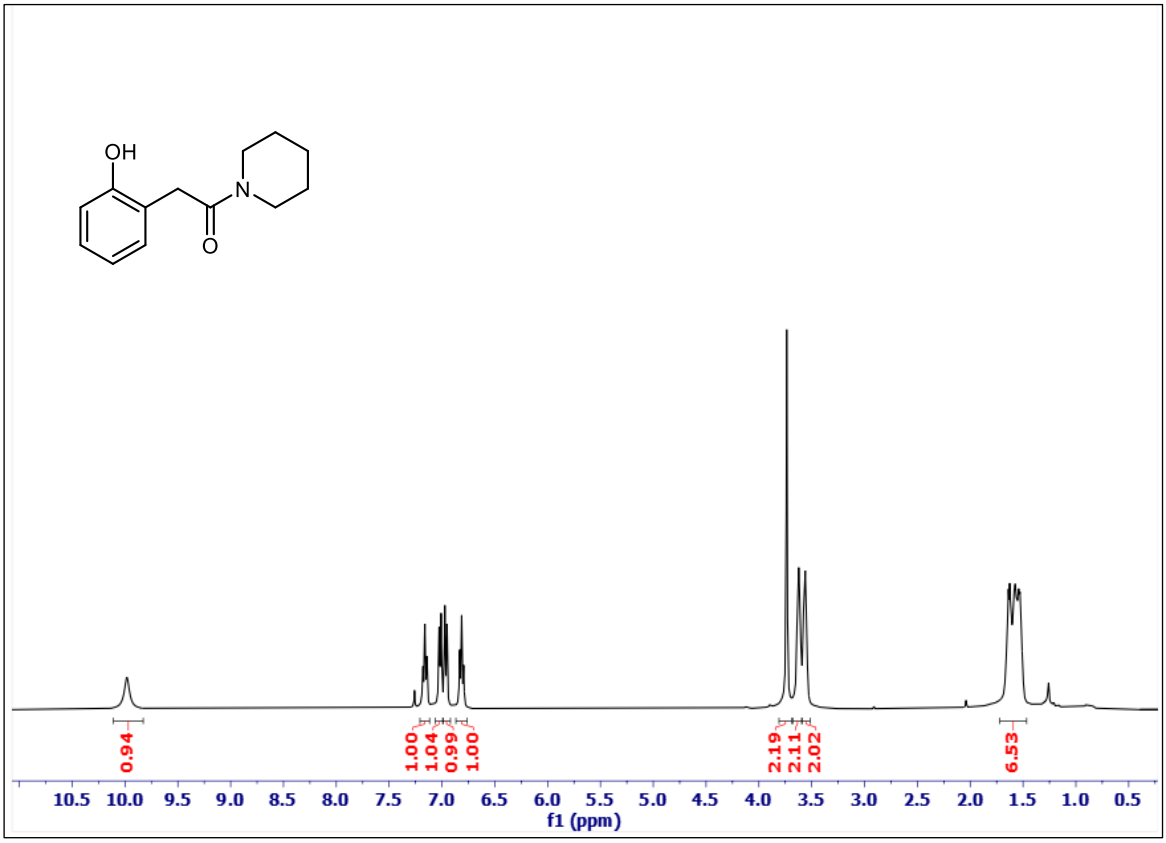


^{13}C NMR (100 MHz, $CDCl_3$)

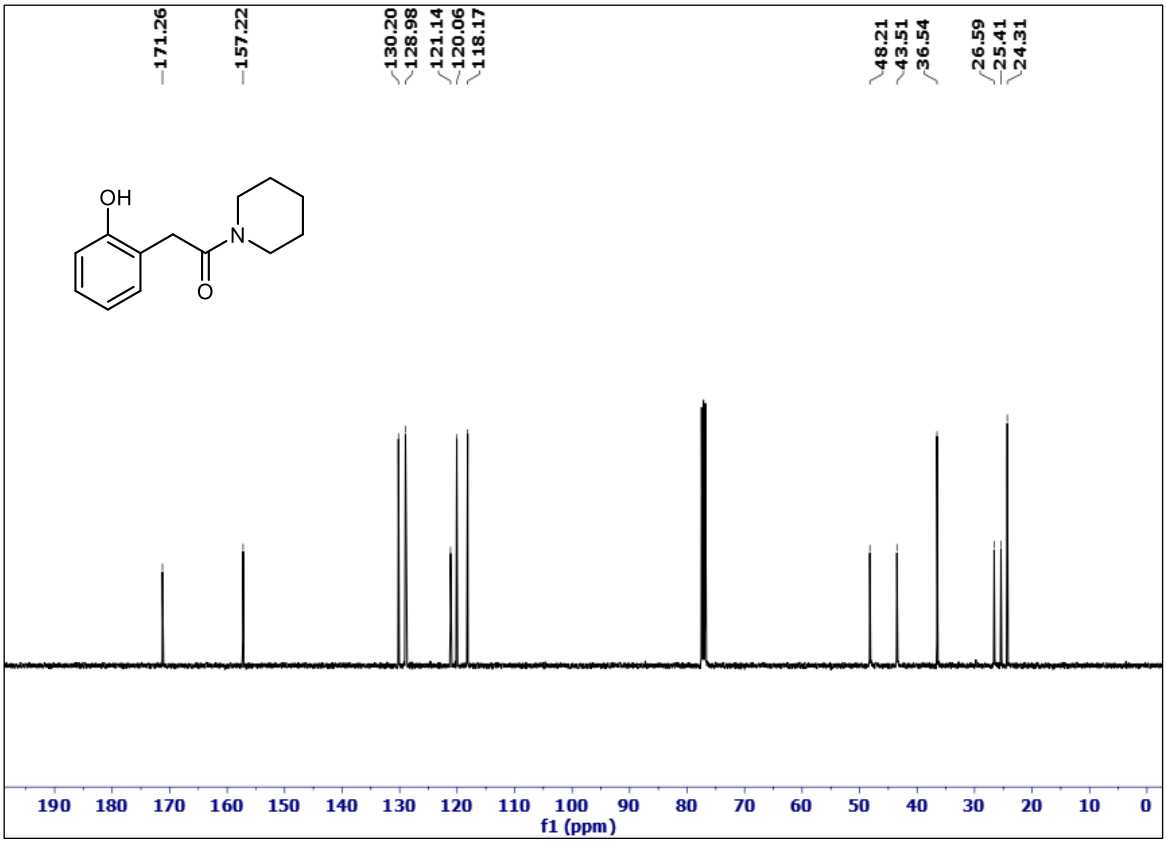


2-(2-Hydroxyphenyl)-1-(piperidin-1-yl)ethan-1-one (2z)

^{1}H NMR (400 MHz, $CDCl_3$)

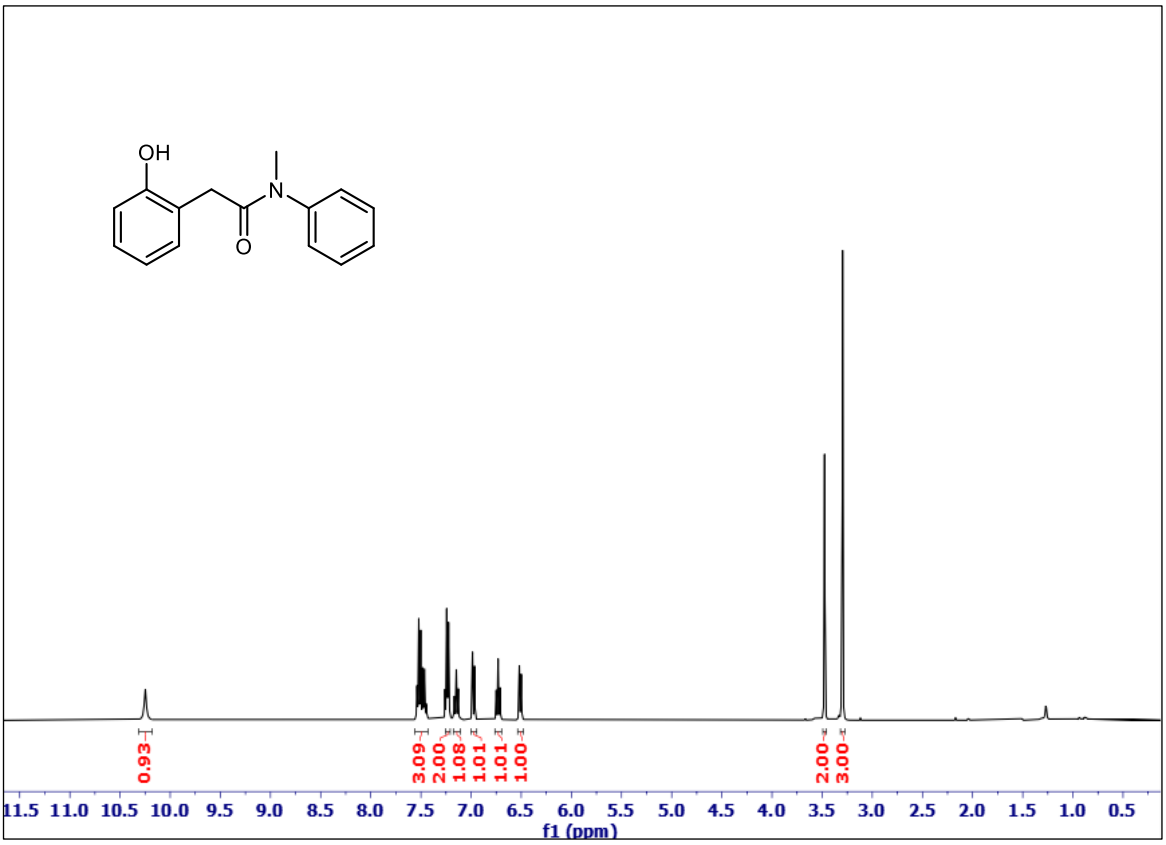


^{13}C NMR (100 MHz, $CDCl_3$)

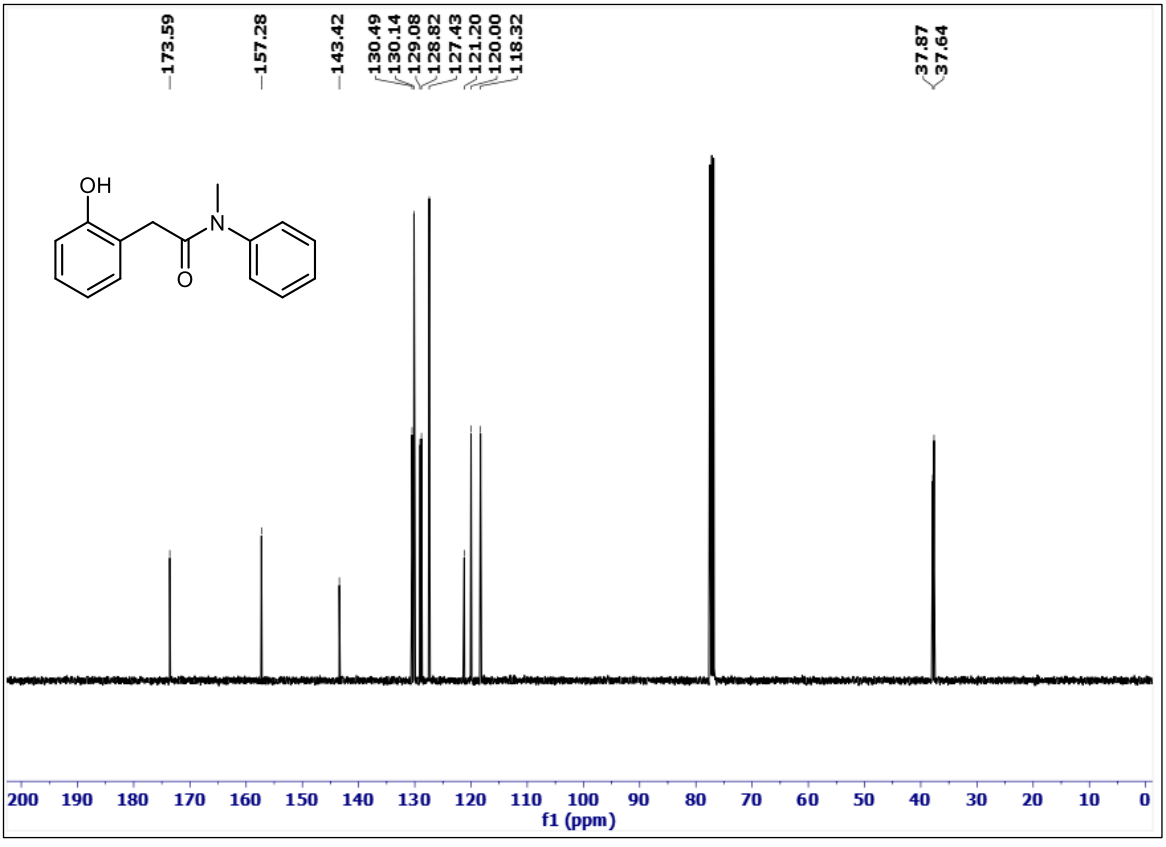


2-(2-Hydroxyphenyl)-*N*-methyl-*N*-phenylacetamide (2ac)

^{1}H NMR (400 MHz, $CDCl_3$)

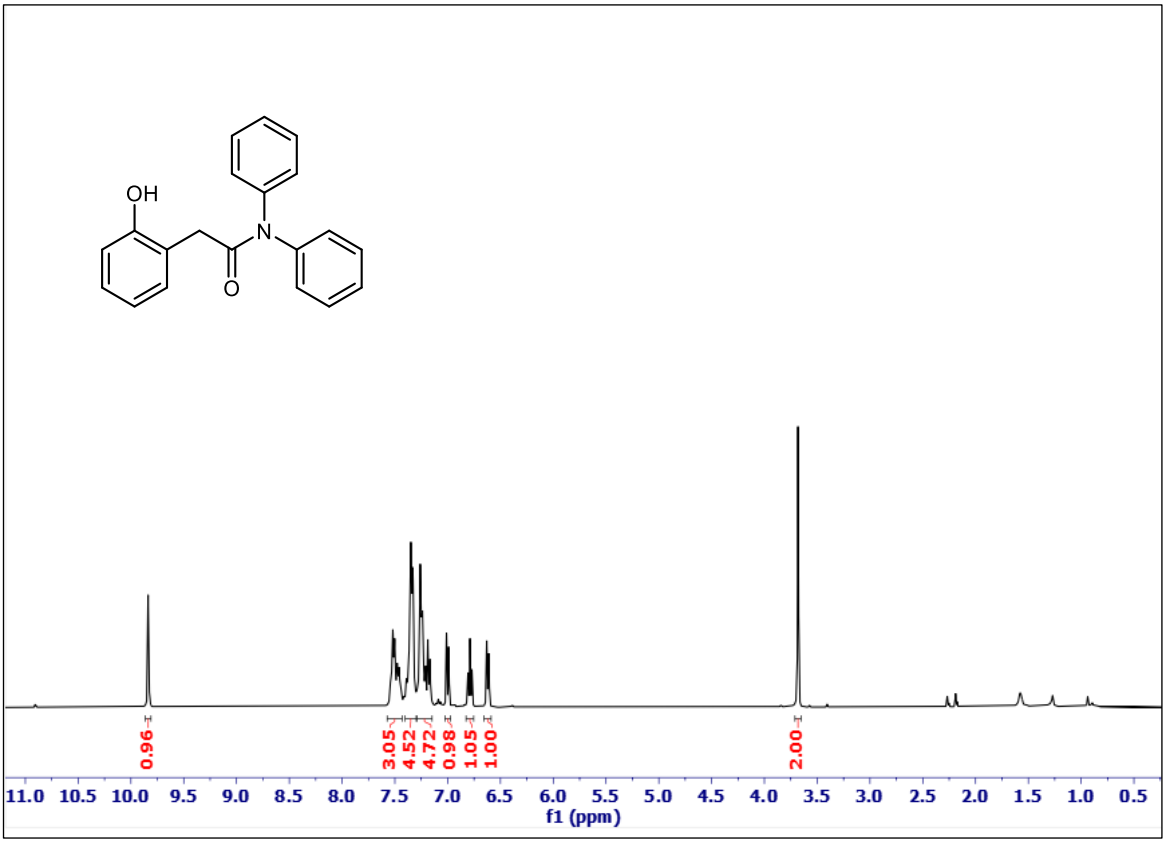


^{13}C NMR (100 MHz, $CDCl_3$)

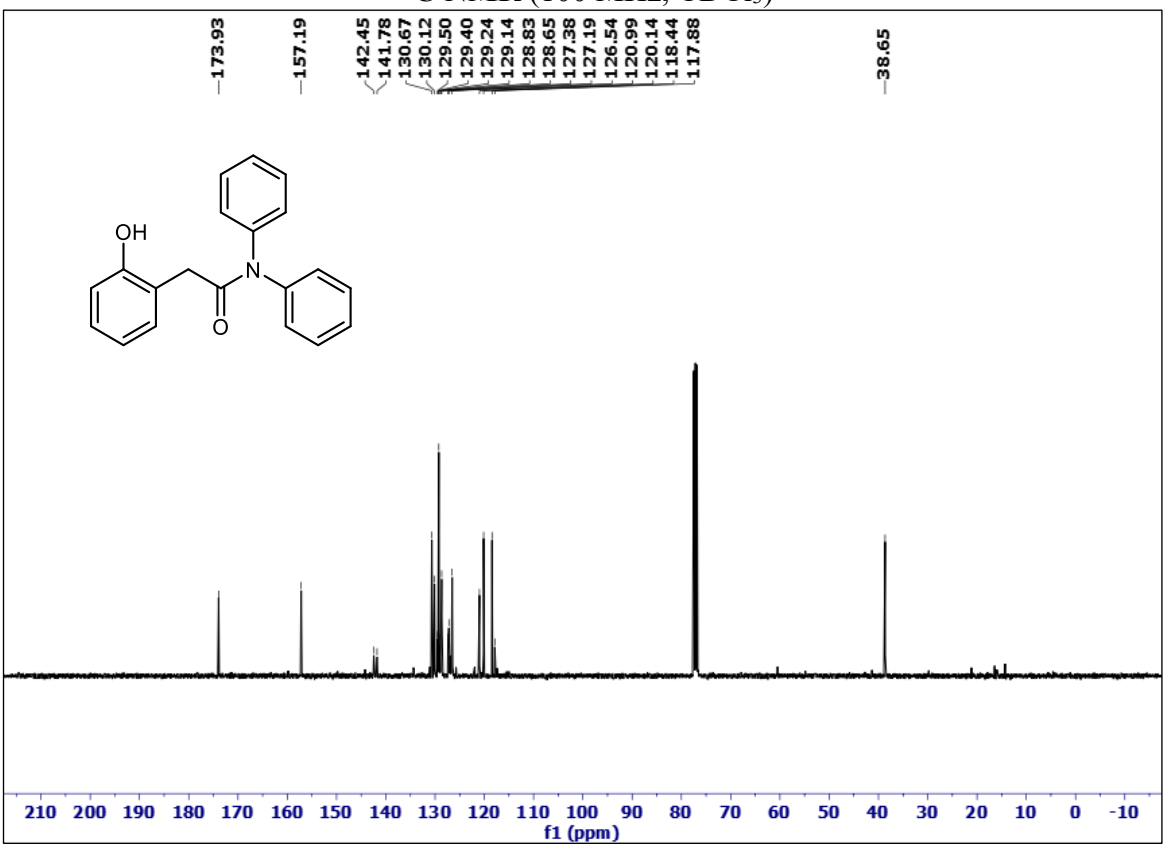


2-(2-Hydroxyphenyl)-*N,N*-diphenylacetamide (2ad)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



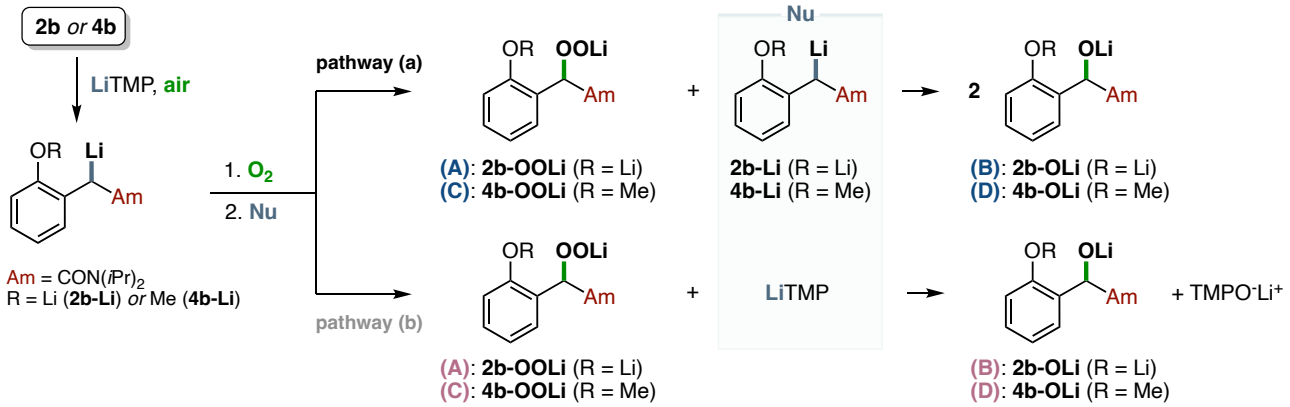
Computational investigations

Method. The stationary points on the energy hypersurface were optimized with DFT M06-2X functional.[14] The polarized def2-SVP basis set was used in the DFT optimizations and in the vibrational analysis (both including solvent effects).[15] The molecules were considered as a solute in a polarized continuum (THF), within the Solvation Model based on Density (SMD)[16] and Integral Equation Formalism-Polarizable Continuum Model (IEF-PCM) schemes.[17]

For a better energy assessment, single point calculation with def2-TZVP were carried out. The Gibbs free energies in solution (ΔG) were estimated at $T = 298$ K.

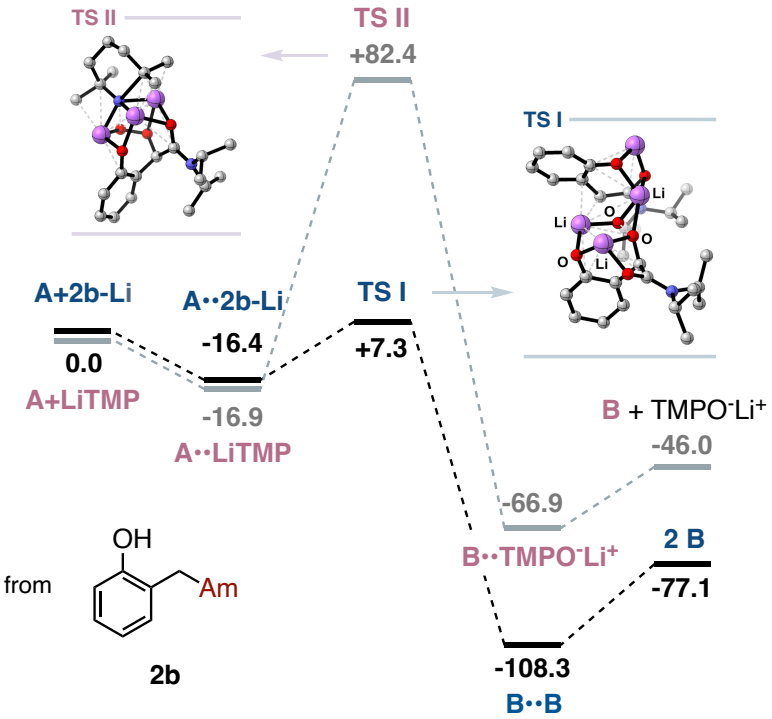
Geometry optimizations and thermochemistry calculations were carried out by using the Gaussian 16 programs.[18] Structures were realised with CYLView20 (Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org).

Nucleophilic cleavage of the lithium hydroperoxide salt



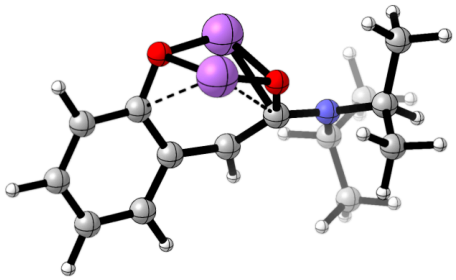
Energies and cartesian coordinates

From compound **2b**



Pathway (a)

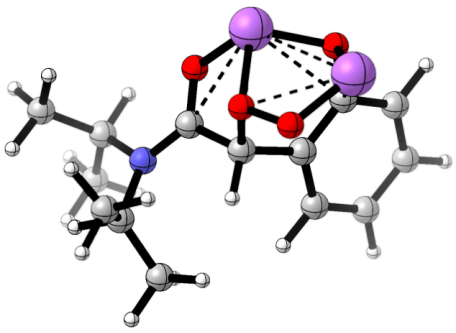
2b-Li (from compound **2b**)



Atom	X	Y	Z	(Angstrom)
6	4.752224	0.356600	0.280029	
6	4.058394	-0.704387	-0.291067	
6	2.660972	-0.666216	-0.500290	
6	1.930952	0.486342	-0.055942	
6	2.674064	1.547530	0.503090	
6	4.054327	1.501828	0.673708	
1	5.834993	0.294447	0.409297	
1	4.582923	-1.599720	-0.633257	
1	2.126796	2.439883	0.820324	
1	4.579641	2.350300	1.115815	
8	2.055227	-1.692333	-1.084084	
6	0.475855	0.679466	-0.207788	
1	0.181179	1.726631	-0.267807	
6	-0.538263	-0.251782	-0.020618	
8	-0.302720	-1.518388	0.216096	
7	-1.887751	0.070276	-0.177472	
6	-2.885985	-0.663518	0.619373	
6	-2.498260	-0.794663	2.092587	
6	-3.270408	-2.008197	0.004251	
1	-3.786194	-0.033426	0.593309	
1	-3.342524	-1.200418	2.669971	
1	-1.638169	-1.465821	2.213895	
1	-2.237058	0.187996	2.513464	
1	-3.564654	-1.879919	-1.048369	
1	-2.424168	-2.705337	0.049996	
1	-4.123149	-2.446606	0.545469	
6	-2.289315	1.379243	-0.693893	
6	-2.500382	2.416342	0.411075	
6	-3.513103	1.273692	-1.604451	
1	-1.462912	1.716753	-1.332591	
1	-2.710707	3.406653	-0.019836	
1	-3.355269	2.141185	1.049193	
1	-1.608125	2.500736	1.048906	
1	-4.423269	0.989454	-1.055688	
1	-3.706484	2.247883	-2.077057	
1	-3.342570	0.534412	-2.400729	
3	1.309214	-2.283211	0.509842	
3	0.339944	-1.491767	-1.599335	

Energy -764.464107 (Hartree)

2b-OOLi (A) (from compound **2b**)

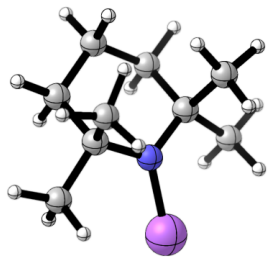


Atom	X	Y	Z	(Angstrom)
6	3.553106	-2.196498	-0.109776	
6	3.609650	-0.984755	-0.788692	
6	2.629157	0.019830	-0.614945	
6	1.571728	-0.248937	0.305431	
6	1.541998	-1.471433	0.981611	

6	2.513550	-2.452246	0.786553
1	4.329975	-2.945952	-0.278157
1	4.419924	-0.769464	-1.488604
1	0.728686	-1.658787	1.686312
1	2.461861	-3.396189	1.330629
8	2.738481	1.170808	-1.257803
3	3.136822	2.286167	0.156654
6	0.408417	0.719677	0.535564
1	0.062469	0.601915	1.569478
6	-0.668741	0.402170	-0.510073
8	-0.362661	0.668111	-1.685364
7	-1.837915	-0.160961	-0.174656
6	-2.707650	-0.626811	-1.276568
6	-3.821977	0.372731	-1.569377
6	-3.229355	-2.032924	-1.001562
1	-2.054473	-0.671450	-2.154418
1	-4.403419	0.036760	-2.440083
1	-4.517790	0.470220	-0.721616
1	-3.404181	1.363832	-1.797856
1	-2.398251	-2.725099	-0.804191
1	-3.925115	-2.065569	-0.149647
1	-3.773367	-2.395238	-1.885564
6	-2.461112	-0.071729	1.167826
6	-2.531177	1.368916	1.671020
6	-1.913687	-1.052886	2.202020
1	-3.497924	-0.379413	0.984442
1	-3.108362	1.401430	2.606431
1	-1.540231	1.800037	1.870392
1	-3.037390	2.007121	0.932355
1	-0.967577	-0.717960	2.647858
1	-2.641724	-1.147801	3.020653
1	-1.765713	-2.048010	1.759220
8	0.692176	2.073715	0.288148
8	1.711789	2.513266	1.194946
3	1.095271	1.876676	-1.642871

Energy -914.679406 (Hartree)

LiTMP

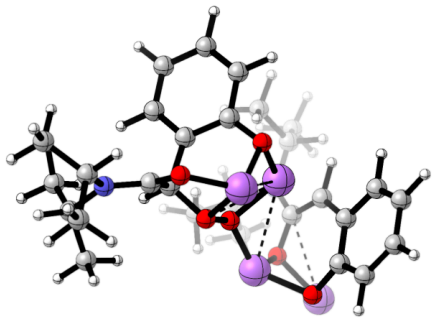


Atom	X	Y	Z	(Angstrom)
6	-1.248034	1.153962	-0.704473	
6	-1.246893	-0.201420	0.039359	
6	1.247090	-0.202115	0.039246	
6	1.248789	1.153339	-0.704573	
6	0.000592	1.974564	-0.395844	
1	-1.269539	0.944732	-1.789106	
1	-2.161906	1.724568	-0.464509	
1	2.162967	1.723490	-0.464746	
1	1.270053	0.944015	-1.789195	
1	0.000731	2.279247	0.664401	
1	0.000774	2.906948	-0.982878	
7	-0.000053	-0.923787	-0.159972	

6	-1.624174	0.040996	1.522617	
1	-2.670343	0.376459	1.618761	
1	-1.507179	-0.895748	2.089999	
1	-0.994794	0.803027	2.000743	
6	-2.367657	-1.067374	-0.552113	
1	-2.428652	-2.034399	-0.020848	
1	-3.353676	-0.584263	-0.466420	
1	-2.179076	-1.262583	-1.621374	
6	2.367500	-1.068398	-0.552351	
1	3.353594	-0.585305	-0.467255	
1	2.428443	-2.035259	-0.020854	
1	2.178269	-1.264044	-1.621393	
6	1.624443	0.039956	1.522516	
1	1.507484	-0.897000	2.089588	
1	2.670627	0.375325	1.618781	
1	0.994898	0.801625	2.000938	
3	-0.004081	-2.598463	-0.847044	

Energy -415.587752 (Hartree)

A••2b-Li (complex)

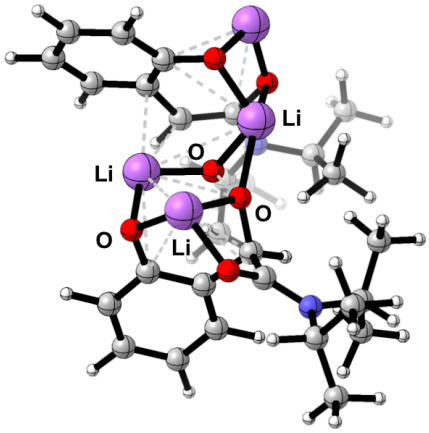


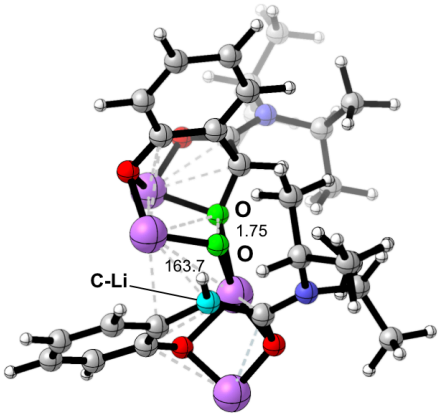
Atom	X	Y	Z	(Angstrom)
6	-0.710509	2.055593	3.478637	
6	-0.390750	0.717228	3.285682	
6	-0.709384	0.032183	2.088021	
6	-1.398130	0.770361	1.076839	
6	-1.690914	2.120614	1.288277	
6	-1.359533	2.776157	2.473524	
1	-0.441799	2.544514	4.418074	
1	0.132892	0.147757	4.056802	
1	-2.193613	2.676885	0.494501	
1	-1.602047	3.831192	2.606554	
8	-0.321373	-1.214856	1.918014	
3	1.096547	-0.905115	0.726177	
6	-1.880719	0.131246	-0.225372	
1	-1.947292	0.913907	-0.990624	
6	-3.224243	-0.559336	0.051170	
8	-3.165946	-1.577008	0.760187	
7	-4.381819	-0.056105	-0.401600	
6	-5.628316	-0.655418	0.124721	
6	-6.221876	-1.661521	-0.855982	
6	-6.621055	0.424632	0.539981	
1	-5.323599	-1.200119	1.024466	
1	-7.102446	-2.142898	-0.406570	
1	-6.546572	-1.179453	-1.791105	
1	-5.489884	-2.445131	-1.099177	
1	-6.158601	1.128467	1.246688	
1	-7.012263	0.991407	-0.318053	
1	-7.478165	-0.048271	1.040339	
6	-4.519290	0.812069	-1.595850	

6	-3.827092	0.215609	-2.819883
6	-4.188087	2.285641	-1.370181
1	-5.594471	0.777147	-1.809173
1	-4.068499	0.819102	-3.706814
1	-2.732960	0.191072	-2.718262
1	-4.177435	-0.811529	-2.996312
1	-3.109102	2.487971	-1.404477
1	-4.653810	2.879712	-2.169743
1	-4.585285	2.635908	-0.407137
8	-1.083841	-0.933073	-0.705449
8	0.249130	-0.471758	-0.849965
3	-1.380789	-2.203639	0.818690
6	3.267040	0.314221	-0.758712
6	3.238490	-0.663480	0.250424
8	3.067577	0.068466	-2.020142
7	3.504850	1.648015	-0.467469
6	3.010929	-2.128782	0.251124
1	3.435111	-0.307000	1.259695
3	1.442518	-0.947899	-2.135172
3	3.805943	-1.476384	-2.629634
6	3.045945	2.680766	-1.414920
6	3.794289	2.108568	0.893103
6	2.595405	-2.974770	-0.842504
6	3.126272	-2.750768	1.520223
8	2.451801	-2.532569	-2.078702
6	1.602811	2.503158	-1.897846
6	4.016330	2.891210	-2.575015
1	3.047950	3.607618	-0.826936
6	2.518168	2.476988	1.652574
6	4.818279	3.244238	0.915065
1	4.282500	1.274239	1.408463
6	2.334763	-4.338118	-0.574238
6	2.867950	-4.097465	1.754459
1	3.435458	-2.123959	2.362148
1	1.207202	3.474381	-2.233136
1	1.541808	1.797513	-2.735882
1	0.961443	2.121098	-1.089344
1	5.029181	3.105802	-2.203004
1	4.055233	1.991939	-3.203207
1	3.691700	3.742075	-3.194114
1	2.739845	2.724664	2.701793
1	2.028047	3.351861	1.195807
1	1.798276	1.643721	1.643738
1	4.423906	4.184946	0.503981
1	5.115413	3.442878	1.955242
1	5.719767	2.965976	0.349951
6	2.464355	-4.904219	0.689311
1	2.022631	-4.941933	-1.429455
1	2.979236	-4.506350	2.760096
1	2.250817	-5.964646	0.840136

Energy -1679.203509 (Hartree)

TS I (from **A••2b-Li** complex)



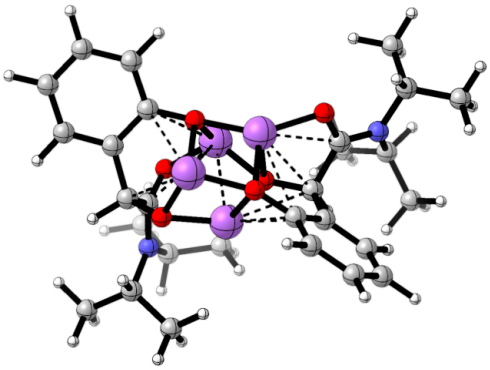


Atom	X	Y	Z	(Angstrom)
6	-1.097640	-0.849413	4.334423	
6	-0.576286	-1.791572	3.454222	
6	-0.706118	-1.669411	2.049410	
6	-1.384586	-0.511660	1.557276	
6	-1.899539	0.418633	2.463180	
6	-1.772642	0.269508	3.844653	
1	-0.974066	-0.990299	5.410894	
1	-0.048666	-2.672895	3.826318	
1	-2.407805	1.301553	2.068204	
1	-2.183845	1.019263	4.521986	
8	-0.173562	-2.586035	1.262771	
3	1.419334	-1.784187	0.728950	
6	-1.581548	-0.230204	0.061061	
1	-1.648080	0.860300	-0.050059	
6	-2.889396	-0.921633	-0.362998	
8	-2.860687	-2.163853	-0.369063	
7	-3.994242	-0.221853	-0.674707	
6	-5.247758	-0.982412	-0.864368	
6	-5.546832	-1.211804	-2.342648	
6	-6.405333	-0.323288	-0.122234	
1	-5.059504	-1.957790	-0.403359	
1	-6.441251	-1.842729	-2.448574	
1	-5.741687	-0.266447	-2.872647	
1	-4.706418	-1.723917	-2.833118	
1	-6.157295	-0.182501	0.939604	
1	-6.680866	0.651769	-0.551715	
1	-7.290875	-0.972038	-0.183107	
6	-3.995659	1.182028	-1.149669	
6	-3.013089	1.404196	-2.298569	
6	-3.887981	2.241114	-0.053915	
1	-4.997105	1.301018	-1.581649	
1	-3.152770	2.414820	-2.709635	
1	-1.964962	1.312886	-1.980592	
1	-3.192469	0.677195	-3.104070	
1	-2.855245	2.395433	0.288728	
1	-4.244550	3.202309	-0.451964	
1	-4.511708	1.976894	0.811722	
8	-0.611018	-0.767823	-0.778107	
8	0.942755	-0.282239	-0.148779	
3	-0.999283	-2.621053	-0.369387	
6	2.769383	1.200857	-0.612752	

6	3.040037	0.017005	0.128620
8	2.663984	1.208809	-1.893797
7	2.528514	2.400213	0.016928
6	3.490768	-1.308905	-0.347892
1	3.202533	0.138633	1.197508
3	1.056416	-0.186985	-1.921264
3	3.347478	0.018422	-3.044522
6	1.704951	3.406956	-0.680021
6	2.626263	2.537914	1.475119
6	3.092213	-1.974191	-1.570283
6	4.256291	-2.065753	0.574202
8	2.362193	-1.404827	-2.511292
6	0.416617	2.838436	-1.289811
6	2.506568	4.233642	-1.681493
1	1.379385	4.090977	0.113784
6	1.313482	2.162220	2.164067
6	3.129769	3.919279	1.892205
1	3.406269	1.839431	1.798123
6	3.521129	-3.311099	-1.763046
6	4.651946	-3.381880	0.358006
1	4.548676	-1.574015	1.506669
1	-0.339364	3.634111	-1.375957
1	0.591769	2.425566	-2.292997
1	0.022922	2.036434	-0.647126
1	3.370895	4.706920	-1.192569
1	2.870353	3.593253	-2.495237
1	1.876497	5.028863	-2.109326
1	1.430563	2.149609	3.258532
1	0.525835	2.895384	1.921095
1	0.976973	1.172111	1.820252
1	2.391790	4.716014	1.719036
1	3.350443	3.910875	2.969647
1	4.055355	4.176245	1.356495
6	4.280475	-4.010268	-0.832882
1	3.207196	-3.784848	-2.696072
1	5.242954	-3.906570	1.110368
1	4.574154	-5.042960	-1.033106

Energy -1679.165289 (Hartree)

2b-OLi••2b-OLi (complex from **TS I**)



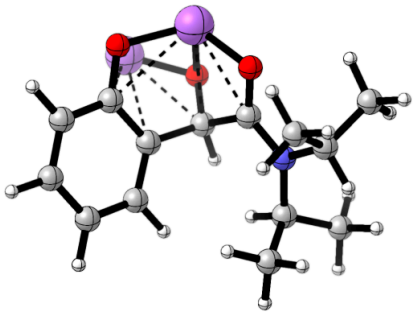
Atom	X	Y	Z	(Angstrom)
6	-3.750075	4.556806	0.096207	
6	-2.465271	4.037663	0.230095	
6	-2.245517	2.654264	0.391577	
6	-3.375445	1.789310	0.430297	
6	-4.653000	2.339412	0.299394	
6	-4.858354	3.709037	0.128002	

6	-3.224099	0.281488	0.625083
6	-2.821357	-0.404496	-0.701504
7	-3.028153	-1.727117	-0.821313
6	-3.620858	-2.547289	0.253874
6	-5.002925	-3.053204	-0.146055
8	-1.013311	2.171819	0.518613
8	-2.234430	0.240440	-1.590101
8	-2.302525	-0.091433	1.586233
3	-0.595881	-0.649025	1.202542
6	-2.625425	-2.433730	-2.056847
6	-3.323108	-1.883062	-3.298260
6	-1.107201	-2.504618	-2.206226
6	-2.683211	-3.678036	0.672131
8	0.545741	-0.081130	-0.175029
3	-0.651410	1.013821	-0.982127
6	1.837575	-0.493465	0.078277
6	2.790874	0.685473	-0.207515
7	3.877524	0.551215	-0.990747
6	4.000395	-0.442078	-2.083556
6	4.470355	-1.828535	-1.648785
6	2.097333	-0.890426	1.547592
6	1.374554	-0.315308	2.638174
6	1.713492	-0.733183	3.946044
6	2.725747	-1.654608	4.182379
6	3.437446	-2.207845	3.114678
6	3.109152	-1.818817	1.818156
8	0.394925	0.554010	2.451933
8	2.517079	1.755144	0.362601
6	4.844987	1.668559	-1.006493
6	6.277029	1.152661	-0.915109
6	4.622631	2.588750	-2.202824
6	2.761002	-0.471333	-2.977292
3	-1.301718	1.273754	2.280805
3	0.712977	1.644180	0.934889
1	2.960271	-1.946146	5.208673
1	1.149984	-0.293938	4.771866
1	3.657999	-2.247006	0.975785
1	4.231820	-2.934836	3.288769
1	2.124611	-1.367425	-0.526834
1	4.631879	2.241468	-0.097637
1	5.307610	3.447260	-2.147139
1	4.812317	2.072404	-3.156797
1	3.592284	2.972683	-2.208563
1	6.402156	0.506361	-0.034395
1	6.580947	0.589709	-1.810534
1	6.963567	2.005389	-0.813408
1	4.807821	-0.035794	-2.705921
1	2.951301	-1.117048	-3.846914
1	1.871076	-0.855190	-2.459034
1	2.532649	0.539778	-3.345650
1	3.669019	-2.426331	-1.193530
1	4.827089	-2.378484	-2.531889
1	5.302352	-1.752989	-0.934348
1	-4.246538	-0.073611	0.872344
1	-2.991305	-3.460219	-1.922765
1	-3.714554	-1.897499	1.127627
1	-5.514465	1.665604	0.335709
1	-0.850341	-3.087910	-3.103034
1	-0.674001	-1.500702	-2.298063
1	-0.651741	-2.999075	-1.335466
1	-4.409749	-1.827511	-3.135310
1	-2.955076	-0.882999	-3.555822
1	-3.139544	-2.557371	-4.147500

1	-3.117880	-4.206033	1.532942
1	-2.527955	-4.417742	-0.127135
1	-1.702692	-3.282868	0.978673
1	-4.953528	-3.727113	-1.015247
1	-5.454082	-3.612949	0.685850
1	-5.666017	-2.212048	-0.396404
1	-1.590200	4.690734	0.206258
1	-5.868856	4.108128	0.028751
1	-3.885926	5.633293	-0.030775

Energy -1679.362591 (Hartree)

2b-OLi (B)



Atom	X	Y	Z	(Angstrom)
6	3.472814	1.644605	1.007591	
6	3.493832	0.255786	1.017570	
6	2.571687	-0.514922	0.266253	
6	1.589987	0.195830	-0.499429	
6	1.614236	1.594552	-0.513332	
6	2.536046	2.331432	0.229591	
1	4.202676	2.199147	1.602347	
1	4.232580	-0.292355	1.606412	
1	0.885998	2.126498	-1.132576	
1	2.527645	3.421926	0.196977	
8	2.667806	-1.830654	0.242921	
3	2.722043	-1.922016	-1.635459	
6	0.508671	-0.580189	-1.284275	
1	0.150638	0.082453	-2.092408	
6	-0.636337	-0.825010	-0.252862	
8	-0.530270	-1.852726	0.440525	
7	-1.661559	0.025623	-0.067749	
6	-2.663619	-0.258749	0.985195	
6	-2.055787	-0.221481	2.384752	
6	-3.453602	-1.535831	0.710692	
1	-3.375462	0.574249	0.923412	
1	-1.362649	-1.057708	2.536538	
1	-1.511192	0.720696	2.544660	
1	-2.857366	-0.286236	3.135304	
1	-4.284934	-1.613334	1.426883	
1	-3.877698	-1.517849	-0.304187	
1	-2.817683	-2.423429	0.811046	
6	-1.872711	1.259455	-0.843563	
6	-1.817263	2.498033	0.048369	
6	-3.161073	1.186938	-1.659674	
1	-1.047150	1.334518	-1.555095	
1	-2.667237	2.542344	0.745721	
1	-0.885045	2.517786	0.631207	
1	-1.853817	3.402622	-0.576201	
1	-3.256316	2.089166	-2.280994	
1	-3.150314	0.310178	-2.323346	

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  1    -4.053084     1.129591    -1.017807
  8     0.937199    -1.789921    -1.777567
  3     1.035346    -2.689953    -0.108524
Energy          -839.636707  (Hartree)
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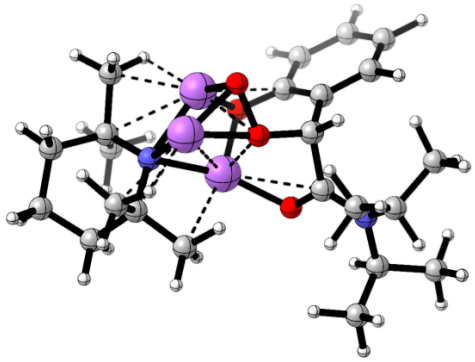
Pathway (b)

A••LiTMP (complex)



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Atom       X             Y             Z        (Angstrom)
  6     0.609367     2.515235    -0.511870
  6     1.597649     1.881691     0.302007
  6     2.802467     2.535494     0.573349
  6     3.094067     3.796636     0.055947
  6     2.140803     4.421815    -0.752260
  6     0.929266     3.798231    -1.023197
  6     1.424630     0.467715     0.838234
  6     1.750787    -0.516374    -0.298782
  8     0.955178    -0.549211    -1.245942
  8    -0.555577     1.974713    -0.761682
  8     0.107566     0.103375     1.183483
  8    -0.470606     0.995621     2.164890
  7     2.877537    -1.250312    -0.274404
  6     3.225502    -1.982560    -1.511189
  6     2.784979    -3.441042    -1.434833
  6     3.599680    -1.652566     0.955231
  6     2.667333    -2.266669     1.998487
  6     4.539581    -0.593608     1.527178
  6     4.704380    -1.825093    -1.847201
  3    -1.669312    -0.396624     1.928381
  3    -0.821997     0.125653    -0.861425
  3    -1.517961     1.579790     0.743020
  7    -2.641822    -0.145480     0.191404
  6    -3.808435     0.709158    -0.144526
  6    -5.152838     0.027458     0.171098
  6    -3.997821    -1.966710    -0.897539
  6    -2.886739    -1.610151     0.103019
  6    -3.793287     1.156808    -1.623254
  6    -3.775242     2.006218     0.693476
  6    -1.610172    -2.325159    -0.367462
  6    -3.261885    -2.238466     1.475586
  1     2.342130     5.410971    -1.170852
  1     0.174956     4.284294    -1.645716
  1     3.534275     2.037499     1.213748
  1     4.043033     4.283153     0.284658
  1     2.080820     0.344727     1.707514
  1     2.645833    -1.495867    -2.302525
  1     2.987912    -3.943829    -2.391490
  1     3.326029    -3.989430    -0.647840
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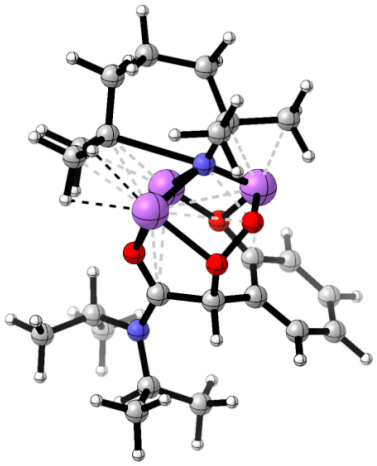
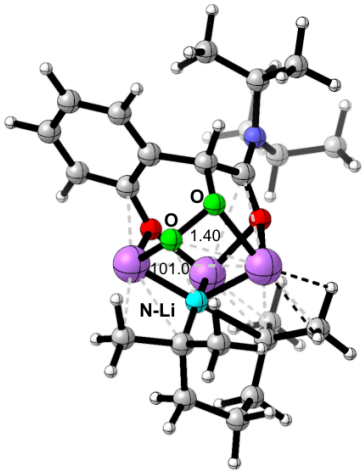
1	1.705508	-3.508414	-1.233943
1	4.981400	-0.762308	-1.896888
1	5.360709	-2.326801	-1.120459
1	4.899174	-2.274834	-2.831330
1	4.244077	-2.471154	0.611734
1	3.265012	-2.687493	2.820000
1	1.972260	-1.534712	2.433243
1	2.076461	-3.079902	1.552104
1	4.013632	0.165283	2.121772
1	5.264905	-1.082401	2.193709
1	5.096239	-0.089305	0.724843
1	-4.106798	-3.062009	-0.943471
1	-3.656976	-1.648921	-1.893994
1	-5.203230	-0.121883	1.261512
1	-5.974433	0.716322	-0.081256
1	-2.841944	1.668327	-1.840085
1	-3.887484	0.306237	-2.312030
1	-4.616235	1.858117	-1.841404
1	-4.716124	2.564543	0.583815
1	-3.643107	1.788712	1.766890
1	-2.998687	2.718169	0.356056
1	-1.351841	-2.033565	-1.399169
1	-0.745730	-2.096907	0.277955
1	-1.744410	-3.417941	-0.362662
1	-4.110850	-1.724887	1.946462
1	-3.521229	-3.303819	1.372857
1	-2.416961	-2.230295	2.193074
6	-5.339769	-1.309353	-0.558525
1	-5.913369	-1.160062	-1.486091
1	-5.945460	-1.983772	0.066506

Energy -1330.334974 (Hartree)

TS II (from **A••LITMP** complex)



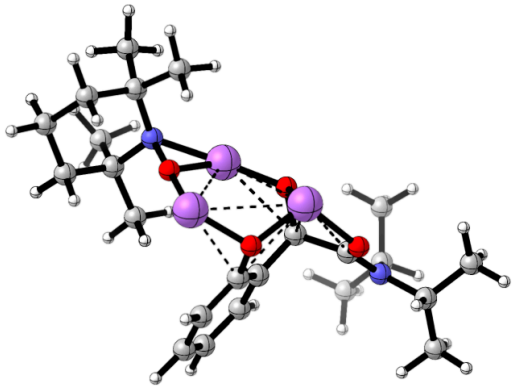


Atom	X	Y	Z	(Angstrom)
6	-1.138439	1.656645	1.240397	
6	-1.593269	1.731472	-0.109136	
6	-2.431320	2.778546	-0.504341	
6	-2.906179	3.722186	0.401775	
6	-2.533705	3.607677	1.745861	
6	-1.669331	2.601379	2.156727	
6	-1.192678	0.682296	-1.126025	
6	-1.247744	-0.742378	-0.534125	
8	-0.162500	-1.316190	-0.314619	
8	-0.202878	0.816479	1.603532	

8	0.098055	0.837006	-1.729792
8	0.951196	1.762711	-1.107340
7	-2.409617	-1.328581	-0.218040
6	-2.343388	-2.515111	0.670226
6	-2.500029	-3.818141	-0.104596
6	-3.719812	-1.099074	-0.877856
6	-3.649700	-1.353512	-2.382118
6	-4.426555	0.207284	-0.533878
6	-3.334902	-2.379706	1.821544
3	1.410492	-0.791012	-1.252116
3	1.087747	1.892038	0.751847
3	1.038802	-0.471160	1.024486
1	-2.910501	4.324698	2.479117
1	-1.346240	2.526590	3.197227
1	-2.731396	2.839198	-1.554278
1	-3.563597	4.526575	0.070167
1	-1.908547	0.750428	-1.957846
1	-1.337147	-2.497032	1.099934
1	-2.373721	-4.670113	0.578927
1	-3.496287	-3.905621	-0.564892
1	-1.737919	-3.896403	-0.893430
1	-3.194876	-1.420458	2.340908
1	-4.383096	-2.455327	1.496640
1	-3.155528	-3.189336	2.543413
1	-4.344179	-1.899352	-0.464844
1	-4.667320	-1.341397	-2.798703
1	-3.067595	-0.587187	-2.913236
1	-3.202989	-2.335521	-2.592327
1	-4.079893	1.040639	-1.155526
1	-5.502629	0.080222	-0.722592
1	-4.287869	0.477171	0.522579
6	2.717833	-1.876929	0.621976
6	3.450084	1.228882	-0.523337
6	4.135195	-1.700457	1.114686
6	4.594009	0.706896	0.377604
6	5.013405	-0.757779	0.296637
1	4.644795	-2.695991	1.166649
1	4.121554	-1.327411	2.156101
1	5.465006	1.333331	0.121801
1	4.337790	0.944620	1.425321
1	6.047515	-0.828211	0.671917
1	5.058700	-1.086367	-0.755427
6	3.362510	2.741346	-0.225513
1	2.594713	3.225841	-0.844297
1	3.143378	2.918286	0.843869
1	4.323886	3.234820	-0.433050
6	3.800128	1.043294	-2.007350
1	2.994776	1.476852	-2.617945
1	4.749376	1.534268	-2.275732
1	3.888675	-0.025335	-2.258515
6	2.710068	-2.662412	-0.681664
1	3.220125	-2.140185	-1.514418
1	3.237391	-3.641203	-0.585757
1	1.686775	-2.923162	-1.014284
6	1.923534	-2.653720	1.666700
1	1.882338	-2.135261	2.643129
1	0.886012	-2.858779	1.348822
1	2.378559	-3.652359	1.875757
7	2.185272	0.570969	-0.192993

Energy -1330.168343 (Hartree)

2b-OLi••LiOTMP (complex from **TS II**)

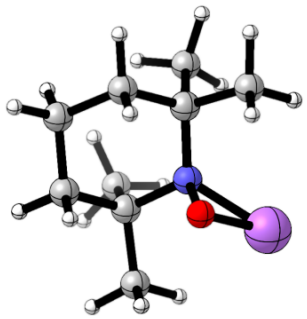


Atom	X	Y	Z	(Angstrom)
6	1.262910	2.097808	0.881740	
6	1.078081	1.132716	-0.111516	
6	0.440273	1.513647	-1.336660	
6	0.044856	2.869286	-1.467508	
6	0.247195	3.807249	-0.459534	
6	0.861012	3.427114	0.732871	
6	1.496913	-0.325700	0.177650	
6	2.843368	-0.555958	-0.546657	
8	2.782084	-0.724597	-1.774125	
8	0.162851	0.670644	-2.312219	
3	-1.667364	0.626077	-2.224133	
8	0.593008	-1.266093	-0.264976	
3	-1.175877	-1.030238	-0.014244	
8	-2.465952	-0.089735	-0.897215	
7	4.029055	-0.519195	0.102663	
6	5.249235	-0.487183	-0.728331	
6	5.847857	-1.878834	-0.911718	
6	4.210628	-0.905885	1.519498	
6	3.532629	-2.238645	1.836749	
6	3.902521	0.187190	2.541116	
3	0.922650	-0.983073	-2.084384	
6	6.257531	0.520300	-0.185383	
1	-0.078710	4.839428	-0.608598	
1	-0.425744	3.163698	-2.410242	
1	1.725097	1.789725	1.822183	
1	1.019959	4.146351	1.537552	
1	1.658587	-0.374369	1.267436	
1	4.914417	-0.135468	-1.710173	
1	6.710620	-1.831104	-1.592309	
1	6.199722	-2.300597	0.042895	
1	5.104989	-2.562873	-1.346613	
1	5.793216	1.510121	-0.068533	
1	6.680259	0.214244	0.783579	
1	7.093769	0.615880	-0.893036	
1	5.289980	-1.088271	1.598553	
1	3.752195	-2.530877	2.874162	
1	2.440914	-2.192154	1.717434	
1	3.911191	-3.027154	1.170016	
1	2.829524	0.271202	2.758073	
1	4.408215	-0.054121	3.487723	
1	4.270062	1.163476	2.194353	
6	-4.206152	-1.557753	-0.348207	
6	-3.556310	0.430369	1.107039	
6	-5.306457	-0.700127	-0.996189	

6	-4.662292	1.262139	0.437229
6	-5.818791	0.397759	-0.064481
1	-6.130269	-1.355538	-1.322512
1	-4.882625	-0.232926	-1.899565
1	-5.019935	2.025120	1.147359
1	-4.214840	1.794683	-0.417333
1	-6.551596	1.025116	-0.594977
1	-6.358898	-0.048002	0.786927
6	-4.014224	-0.111882	2.468996
1	-3.352019	-0.922424	2.806891
1	-3.957015	0.700578	3.207858
1	-5.046362	-0.476365	2.480684
6	-2.330165	1.308069	1.383284
1	-1.528877	0.708504	1.851668
1	-1.932930	1.766639	0.470066
1	-2.600988	2.105033	2.091164
6	-3.575738	-2.476642	-1.398875
1	-3.196592	-1.912602	-2.257703
1	-2.742934	-3.050453	-0.956949
1	-4.326423	-3.196644	-1.755637
6	-4.780074	-2.474070	0.740950
1	-5.296607	-3.315742	0.257319
1	-3.973228	-2.885249	1.365154
1	-5.510699	-1.986653	1.393372
7	-3.120256	-0.675957	0.189615

Energy -1330.413467 (Hartree)

LiOTMP



Atom	X	Y	Z	(Angstrom)
6	1.253253	-1.050417	-0.933313	
6	1.269816	0.014542	0.175963	
6	-1.269791	0.014408	0.175948	
6	-1.253077	-1.050496	-0.933386	
6	0.000114	-1.922581	-0.886979	
1	1.278610	-0.516903	-1.895921	
1	2.165533	-1.665359	-0.863642	
1	-2.165329	-1.665493	-0.863867	
1	-1.278341	-0.516888	-1.895939	
1	0.000090	-2.546843	0.022102	
1	0.000184	-2.622255	-1.737215	
7	-0.000047	0.810429	0.134806	
6	1.515009	-0.616170	1.554323	
1	2.583265	-0.861895	1.648545	
1	1.260385	0.093066	2.356066	
1	0.961369	-1.545171	1.724749	
6	2.426893	0.986280	-0.072458	
1	2.439740	1.775908	0.700745	

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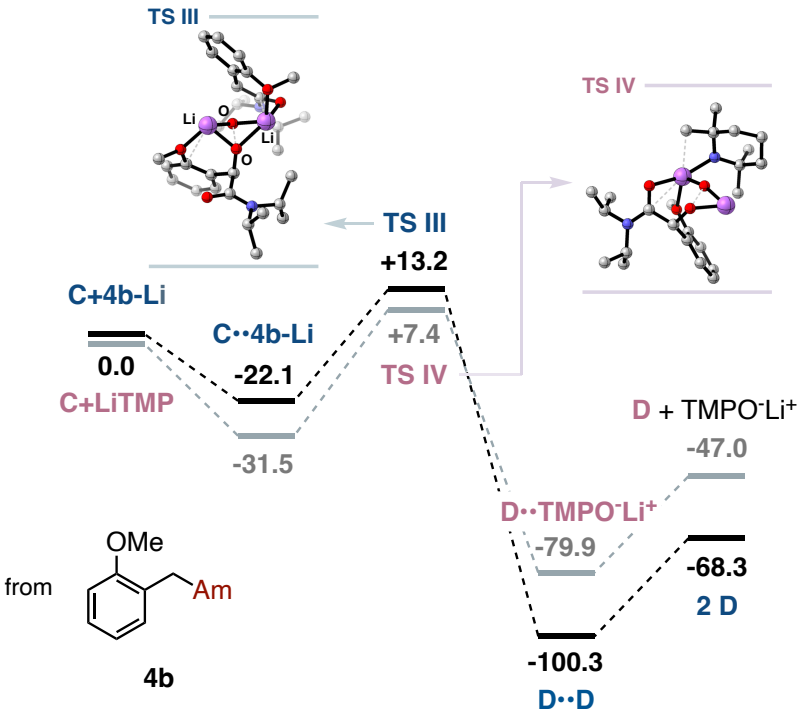
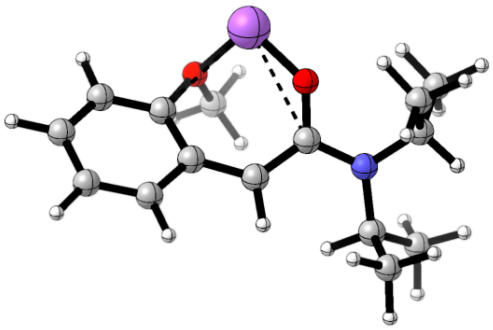
  1     3.384380     0.448171    -0.009686
  1     2.337528     1.456398    -1.056809
  6    -2.427007     0.985995    -0.072385
  1    -3.384430     0.447762    -0.009583
  1    -2.439934     1.775629     0.700805
  1    -2.337750     1.456140    -1.056729
  6    -1.514908    -0.616311     1.554268
  1    -1.261372     0.093402     2.355951
  1    -2.582959    -0.863096     1.648043
  1    -0.960362    -1.544644     1.725230
  8    -0.000113     1.566494    -1.062035
  3    -0.000395     2.708540     0.229304
Energy         -490.713099  (Hartree)
```

From compound **4b**



Pathway (a)

4b-Li (from compound **4b**)

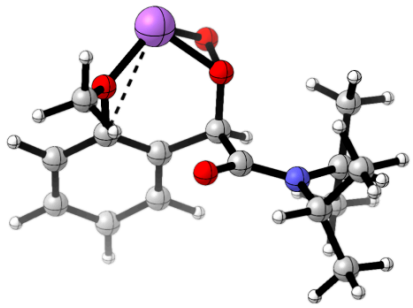


Atom	X	Y	Z	(Angstrom)
6	0.619126	-0.168362	-0.222389	
6	-0.388685	0.784401	0.027573	
8	0.409409	-1.320172	-0.734823	
7	1.945482	0.138934	0.056900	
6	-1.819986	0.624640	-0.092630	
1	-0.075024	1.819481	0.156385	
3	-0.979158	-2.340733	-0.914965	
6	3.025040	-0.546381	-0.667137	
6	2.317903	1.308603	0.851990	
6	-2.594850	-0.549859	0.115494	
6	-2.597107	1.778590	-0.402872	
8	-2.010261	-1.748908	0.519065	
6	2.844566	-0.510400	-2.185196	
6	3.292009	-1.959822	-0.150315	
1	3.927188	0.045121	-0.455128	
6	2.725373	2.498646	-0.018253	
6	3.391563	0.976552	1.889715	
1	1.420876	1.585268	1.418889	
6	-3.981145	-0.580211	-0.047049	

6	-3.974451	1.758291	-0.550131
1	-2.059917	2.718958	-0.549534
1	3.752281	-0.886698	-2.680791
1	1.992084	-1.127356	-2.494865
1	2.670766	0.521153	-2.527294
1	3.455128	-1.948503	0.937678
1	2.436561	-2.611487	-0.367296
1	4.192343	-2.378314	-0.626551
1	2.923319	3.386842	0.600428
1	3.643195	2.275280	-0.585508
1	1.930423	2.747550	-0.736891
1	4.359418	0.726584	1.429860
1	3.554016	1.846209	2.543426
1	3.075465	0.130815	2.517630
6	-4.690034	0.564751	-0.391109
1	-4.488922	-1.531041	0.129116
1	-4.499242	2.682346	-0.802117
1	-5.772992	0.533228	-0.515459
6	-1.521878	-1.751893	1.856698
1	-1.052742	-2.727983	2.031253
1	-0.782552	-0.951697	2.006204
1	-2.360427	-1.618738	2.556894

Energy -796.703769 (Hartree)

4b-OOLi (C) (from compound **4b**)

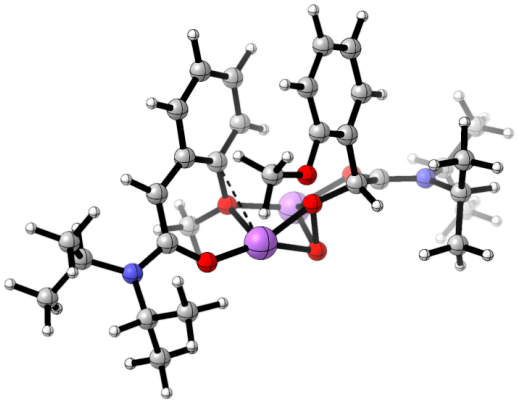


Atom	X	Y	Z	(Angstrom)
6	2.792354	2.571235	0.366320	
6	3.864905	1.791881	0.798037	
6	3.788795	0.404772	0.703959	
6	2.638604	-0.202198	0.197809	
6	1.550011	0.559880	-0.243793	
6	1.658575	1.952373	-0.155227	
8	2.617763	-1.579560	0.082220	
6	0.231695	-0.005441	-0.749196	
8	0.293103	-1.227663	-1.422755	
8	1.077265	-1.040283	-2.627637	
6	-0.714465	-0.271987	0.435357	
7	-2.028877	0.040853	0.296875	
6	-2.675675	0.606525	-0.906495	
6	-2.376266	2.091700	-1.119096	
8	-0.249171	-0.790734	1.441238	
6	-2.919534	-0.278669	1.428529	
6	-3.663658	0.954472	1.932704	
6	-3.862561	-1.428443	1.083386	
6	-2.510373	-0.236767	-2.172104	
3	1.888762	-2.186944	-1.551941	
1	4.766182	2.260654	1.196214	
1	4.624805	-0.224941	1.013915	
1	0.820218	2.561695	-0.503468	

1	2.841569	3.659461	0.425487
1	-0.177137	0.743112	-1.438288
1	-2.249824	-0.618637	2.224995
1	-4.452682	-1.706992	1.968742
1	-4.570420	-1.156150	0.285034
1	-3.293892	-2.311815	0.758119
1	-2.958783	1.754172	2.202748
1	-4.372754	1.348964	1.188800
1	-4.240831	0.691309	2.831038
1	-3.745237	0.555884	-0.665221
1	-3.208669	0.137642	-2.935485
1	-1.496809	-0.214960	-2.593672
1	-2.762715	-1.286675	-1.963642
1	-1.355330	2.277717	-1.479971
1	-3.068460	2.499072	-1.870665
1	-2.518241	2.652567	-0.184380
6	2.583669	-2.301480	1.315055
1	2.545140	-3.367843	1.060323
1	3.493561	-2.107321	1.901107
1	1.688026	-2.013259	1.879969

Energy -946.900062 (Hartree)

C••4b-Li (complex)



Atom	X	Y	Z	(Angstrom)
6	3.039163	1.956296	0.310899	
6	2.104223	1.047584	0.801344	
6	1.024714	1.525723	1.579219	
6	0.908301	2.895834	1.837566	
6	1.866381	3.783435	1.345084	
6	2.937210	3.321721	0.587220	
6	2.146543	-0.437241	0.485244	
6	3.248777	-0.771477	-0.541286	
8	2.933592	-0.657528	-1.735133	
8	0.160787	0.606422	2.054151	
6	-1.033221	1.051376	2.662523	
8	0.932763	-0.726004	-0.141930	
8	0.825653	-2.141026	-0.449420	
7	4.485819	-1.098782	-0.140692	
6	5.536832	-1.224279	-1.174371	
6	5.965707	-2.674838	-1.368422	
6	4.862138	-1.504671	1.234065	
6	4.204132	-2.820763	1.647100	
6	4.742968	-0.399684	2.281096	
6	6.712812	-0.300465	-0.871557	
3	-0.859819	-1.314282	-0.166379	
8	-2.612641	-1.285371	0.024357	
6	-3.538908	-0.430680	-0.150244	

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  7    -4.833984    -0.872995     0.106224
  6    -5.051302    -2.010468     1.009985
  6    -4.312784    -1.872321     2.342428
  6    -3.327788     0.906178    -0.548831
  6    -2.109846     1.548076    -0.991728
  6    -0.982474     0.994624    -1.660854
  6     0.121424     1.765615    -2.032340
  6     0.172279     3.132880    -1.791627
  6    -0.932188     3.728418    -1.171856
  6    -2.019845     2.959534    -0.794329
  8    -0.899113    -0.362463    -1.991372
  6    -1.851867    -0.802974    -2.958846
  6    -6.012784    -0.101354    -0.284426
  6    -6.580577     0.720915     0.873922
  6    -7.085962    -0.980942    -0.928753
  6    -4.787005    -3.361511     0.345876
  3     1.051212    -1.079613    -1.979643
  1     1.763037     4.848994     1.558786
  1     0.072357     3.276073     2.423108
  1     3.870417     1.598039    -0.300005
  1     3.683599     4.015366     0.198545
  1     2.220764    -1.032192     1.404862
  1     5.065149    -0.882940    -2.101156
  1     6.684675    -2.736741    -2.198006
  1     6.457131    -3.081919    -0.471419
  1     5.101578    -3.308627    -1.614670
  1     6.374409     0.737961    -0.742517
  1     7.263827    -0.603805     0.031342
  1     7.420247    -0.325887    -1.712781
  1     5.935489    -1.715122     1.151611
  1     4.598207    -3.135563     2.624256
  1     3.111842    -2.746788     1.730234
  1     4.430655    -3.608465     0.915170
  1     3.707199    -0.189464     2.579480
  1     5.285973    -0.713972     3.184217
  1     5.196939     0.533832     1.918567
  1    -4.139750     1.609502    -0.368572
  1    -6.122934    -1.977124     1.254444
  1    -5.675277     0.589583    -1.066286
  1    -2.865364     3.444599    -0.299707
  1    -4.672995    -2.633707     3.050791
  1    -3.231505    -2.000540     2.208995
  1    -4.497726    -0.880588     2.783368
  1    -5.373445    -3.458737    -0.579930
  1    -3.722714    -3.456655     0.096165
  1    -5.073253    -4.184099     1.019787
  1    -7.416849     1.351067     0.535492
  1    -6.958978     0.064830     1.674260
  1    -5.806944     1.374325     1.304060
  1    -7.528309    -1.695249    -0.218164
  1    -7.901715    -0.348862    -1.309792
  1    -6.667248    -1.545787    -1.774386
  1     0.956312     1.272013    -2.538431
  1    -0.938310     4.802199    -0.971460
  1     1.045132     3.716592    -2.085672
  1    -0.830276     1.587846     3.603496
  1    -1.604628     1.703636     1.982164
  1    -1.624343     0.155232     2.882526
  1    -1.748987    -1.892074    -3.041858
  1    -2.872423    -0.551297    -2.641136
  1    -1.638627    -0.330857    -3.930262
Energy        -1743.673994  (Hartree)
```
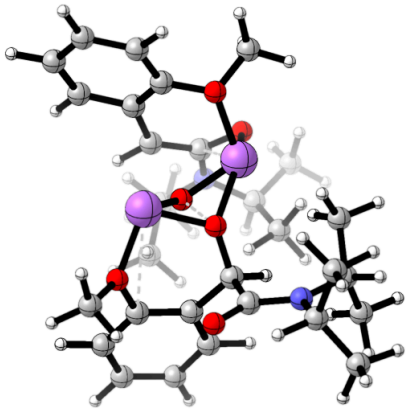
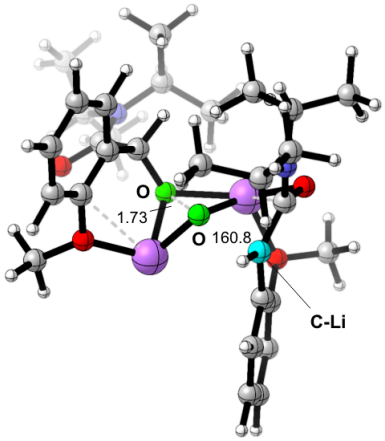

TS III (from **C••4b-Li** complex)



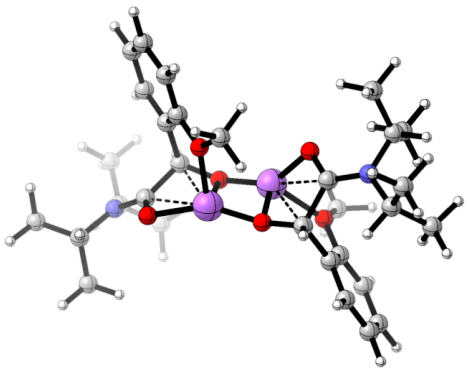


Atom	X	Y	Z	(Angstrom)
6	-2.494011	2.846290	-0.071858	
6	-3.119364	1.703633	0.504191	
6	-3.922792	1.997945	1.642918	
6	-4.115759	3.274331	2.150072	
6	-3.497863	4.371571	1.542811	
6	-2.687630	4.133366	0.438103	
6	-2.961795	0.291805	0.183138	
6	-2.680249	-0.342778	-1.069723	
7	-2.859012	-1.712288	-1.202192	
6	-3.343802	-2.544931	-0.096688	
6	-4.184391	-3.728213	-0.577042	
8	-1.621122	2.750268	-1.144552	
6	-2.172248	3.166407	-2.387274	
8	-2.197874	0.267945	-2.065491	
6	-2.086731	-2.409368	-2.245363	
6	-2.698618	-2.250907	-3.634892	
6	-0.588665	-2.077350	-2.228206	
6	-2.193819	-2.984461	0.813450	
3	-0.674738	1.076103	-1.258741	
8	-0.789391	0.320158	0.364687	
8	0.855059	0.814067	0.187234	
6	1.689897	-0.300894	0.198314	
6	3.106103	0.274554	0.411342	
7	3.854774	0.577951	-0.685377	
6	3.518366	0.283344	-2.091965	
6	3.619190	-1.202176	-2.439854	
6	1.381621	-1.347144	1.256017	
6	0.991336	-1.050231	2.569492	
6	0.722877	-2.066379	3.486359	
6	0.863577	-3.402690	3.114040	
6	1.265207	-3.720249	1.818663	
6	1.508788	-2.694569	0.905534	
8	0.818904	0.263929	2.951439	
6	1.616706	0.707539	4.046197	
8	3.473975	0.509593	1.554044	
6	5.133840	1.276562	-0.457167	
6	6.325588	0.471973	-0.968011	
6	5.098898	2.691999	-1.028486	
6	2.224373	0.923911	-2.602545	
3	-0.113558	1.320078	1.690610	
1	0.651882	-4.191333	3.837934	
1	0.395400	-1.803582	4.493422	
1	1.807135	-2.939876	-0.117302	
1	1.375569	-4.761809	1.513159	

1	1.628833	-0.830295	-0.762674
1	5.219993	1.352224	0.631391
1	6.022663	3.225785	-0.761234
1	5.022028	2.694051	-2.126995
1	4.247217	3.254697	-0.618950
1	6.343867	-0.530147	-0.515541
1	6.315750	0.361604	-2.063450
1	7.259519	0.985675	-0.697118
1	4.321295	0.776824	-2.653945
1	2.256621	0.962468	-3.701047
1	1.335896	0.339041	-2.327195
1	2.114300	1.948111	-2.219988
1	2.827584	-1.801239	-1.966872
1	3.528689	-1.332947	-3.528447
1	4.590070	-1.609270	-2.124347
1	-3.359309	-0.333732	0.976418
1	-2.158875	-3.472372	-1.982582
1	-4.034666	-1.921040	0.480004
1	-4.417804	1.156655	2.133952
1	-0.014549	-2.903455	-2.676843
1	-0.375258	-1.161285	-2.794767
1	-0.253167	-1.931852	-1.190195
1	-3.743160	-2.596612	-3.641086
1	-2.675607	-1.195405	-3.933875
1	-2.135986	-2.846463	-4.370886
1	-2.569907	-3.490225	1.716222
1	-1.535355	-3.692200	0.282977
1	-1.590681	-2.110454	1.109659
1	-3.587953	-4.508791	-1.071396
1	-4.676027	-4.196565	0.288430
1	-4.967076	-3.392458	-1.273106
1	-2.161975	4.954244	-0.055508
1	-4.754646	3.413783	3.024611
1	-3.633270	5.383816	1.925734
1	1.294653	0.237587	4.986650
1	2.672240	0.490557	3.840892
1	1.473668	1.792383	4.126099
1	-1.391155	3.045942	-3.149876
1	-3.034537	2.538634	-2.650049
1	-2.467560	4.226118	-2.343176

Energy -1743.615398 (Hartree)

4b-OLi••4b-OLi (complex from **TS III**)



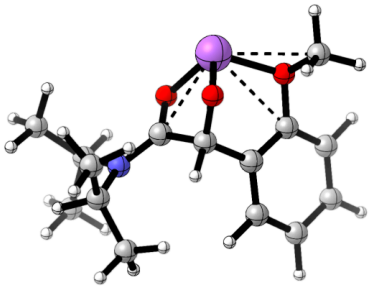
Atom	X	Y	Z	(Angstrom)
6	-3.627917	-2.497981	-1.538899	
6	-2.858825	-1.714876	-0.682408	
6	-2.628585	-2.192025	0.624804	
6	-3.199107	-3.390200	1.059465	

6	-3.986613	-4.140838	0.180784
6	-4.197915	-3.704879	-1.122318
6	-2.213706	-0.400470	-1.141605
8	-0.866603	-0.470514	-1.125601
8	-1.838916	-1.421930	1.426898
6	-1.739196	-1.740604	2.801240
6	-2.702208	0.748153	-0.181774
7	-4.005336	1.096793	-0.112397
6	-5.040855	0.557839	-1.006713
6	-6.031382	-0.326731	-0.252332
8	-1.857965	1.281937	0.545740
6	-4.458177	2.016917	0.950995
6	-4.212543	1.435207	2.342091
6	-3.899385	3.428213	0.788058
6	-5.733505	1.672402	-1.788702
3	0.885030	-0.123829	-1.165805
3	-0.465279	-0.073390	0.691578
8	1.307917	-0.172564	0.730574
6	2.600085	0.232568	0.697003
6	3.325716	-0.528929	-0.443499
7	4.520821	-1.136369	-0.256884
6	4.980995	-1.674667	1.042930
6	5.641539	-0.657881	1.972965
6	2.810352	1.737863	0.411486
6	3.820102	2.424688	1.087805
6	4.051508	3.790254	0.908194
6	3.241729	4.501813	0.030988
6	2.220746	3.850395	-0.662608
6	2.007207	2.478584	-0.486393
8	1.034618	1.823873	-1.173217
6	0.025396	2.562636	-1.832809
8	2.760880	-0.528258	-1.545883
6	5.208310	-1.652043	-1.457514
6	6.697859	-1.326660	-1.420999
6	4.934826	-3.137843	-1.673096
6	3.901952	-2.514187	1.727424
1	3.394644	5.571600	-0.122867
1	1.595141	4.417667	-1.350428
1	4.440254	1.868193	1.792767
1	4.849383	4.289414	1.459802
1	3.139108	0.058180	1.645187
1	4.762470	-1.105943	-2.295837
1	5.395090	-3.472920	-2.614215
1	5.352986	-3.752517	-0.860525
1	3.852965	-3.324188	-1.734450
1	6.857176	-0.247835	-1.279789
1	7.228738	-1.866109	-0.621917
1	7.158362	-1.618115	-2.376097
1	5.776822	-2.376625	0.762911
1	4.301070	-2.947399	2.656424
1	3.006074	-1.927996	1.975761
1	3.589402	-3.338892	1.070333
1	4.910431	-0.060880	2.534208
1	6.258660	-1.192750	2.709938
1	6.295067	0.022765	1.408764
1	-2.629251	-0.182567	-2.151330
1	-5.546601	2.083656	0.820765
1	-4.529186	-0.071390	-1.739515
1	-3.794230	-2.143260	-2.560225
1	-4.382005	4.103658	1.509988
1	-2.816274	3.441597	0.960094
1	-4.101481	3.809591	-0.223959
1	-4.649466	0.427924	2.418138

1	-3.138781	1.371959	2.559280
1	-4.688313	2.073874	3.101020
1	-6.441252	1.234664	-2.507416
1	-6.302253	2.348065	-1.132504
1	-4.997593	2.267352	-2.349010
1	-6.624850	0.253109	0.471422
1	-6.732036	-0.791614	-0.961551
1	-5.504984	-1.129177	0.286428
1	-3.031642	-3.750986	2.073572
1	-4.801347	-4.295427	-1.813190
1	-4.426995	-5.077073	0.528435
1	-0.434741	3.292617	-1.150552
1	0.425676	3.081113	-2.718285
1	-0.726412	1.825852	-2.137737
1	-1.150970	-0.940535	3.266786
1	-2.734110	-1.779866	3.270318
1	-1.222268	-2.700737	2.951221

Energy -1743.804878 (Hartree)

4b-OLi (D)



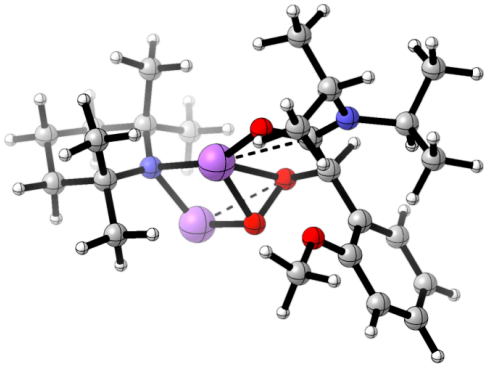
Atom	X	Y	Z	(Angstrom)
6	1.350733	-1.756344	0.646131	
6	1.454326	-0.379967	0.406555	
6	2.558871	0.055058	-0.344182	
6	3.517161	-0.844125	-0.815720	
6	3.392173	-2.206127	-0.555742	
6	2.299817	-2.664500	0.180591	
6	0.344305	0.576602	0.911880	
6	-0.683838	0.585525	-0.253451	
8	-0.316242	1.198749	-1.272327	
8	2.738253	1.392779	-0.655733	
6	3.623547	2.062166	0.243933	
8	0.727072	1.850943	1.153776	
7	-1.884524	-0.023096	-0.183254	
6	-2.694442	-0.083692	-1.416453	
6	-3.755638	1.012050	-1.451055	
6	-2.593698	-0.290414	1.088767	
6	-2.629199	0.949612	1.983462	
6	-2.163524	-1.563491	1.815430	
6	-3.281923	-1.476741	-1.616810	
3	1.039677	2.348582	-0.552156	
1	4.142443	-2.904431	-0.930270	
1	4.354644	-0.453311	-1.397384	
1	0.496391	-2.121015	1.220762	
1	2.186706	-3.728759	0.394001	
1	-0.091696	0.057087	1.787104	
1	-1.985971	0.108740	-2.229425	
1	-4.288155	0.988675	-2.413130	
1	-4.503441	0.880360	-0.653380	
1	-3.292174	2.002864	-1.339102	
1	-2.489953	-2.239353	-1.597975	

1	-4.031559	-1.730357	-0.851862
1	-3.780863	-1.525609	-2.595496
1	-3.630114	-0.468259	0.773987
1	-3.178280	0.726249	2.909992
1	-1.624920	1.309561	2.248159
1	-3.149461	1.770080	1.467262
1	-1.229168	-1.437447	2.378139
1	-2.944428	-1.845074	2.537127
1	-2.040099	-2.394259	1.105768
1	3.179535	2.063950	1.249477
1	4.608203	1.571082	0.249508
1	3.740308	3.091707	-0.119765

Energy -871.857085 (Hartree)

Pathway (b)

C••LiTMP (complex)



Atom	X	Y	Z	(Angstrom)
7	-3.244285	-0.481453	-0.095401	
6	-3.859229	-0.232722	1.210021	
6	-5.364130	-0.575914	1.219374	
6	-6.105102	0.076734	0.057500	
6	-5.449539	-0.332430	-1.256809	
6	-3.942650	0.002252	-1.287243	
6	-3.154710	-1.149289	2.221114	
6	-3.675159	1.211966	1.737260	
6	-3.769096	1.517250	-1.552008	
6	-3.321630	-0.721401	-2.490432	
3	-2.189601	-2.084514	-0.299520	
8	-0.422752	-1.632621	-0.060001	
8	-0.059871	-0.940355	-1.273325	
6	1.235205	-0.410246	-1.156367	
6	1.194221	0.917836	-0.358825	
7	2.292950	1.688871	-0.295213	
6	2.271860	2.919125	0.524663	
6	1.302477	3.970497	-0.010340	
6	2.226594	-1.451169	-0.673324	
6	2.788744	-2.322086	-1.604298	
6	3.653988	-3.348304	-1.218889	
6	3.955173	-3.504107	0.130478	
6	3.406564	-2.645818	1.085369	
6	2.541706	-1.617683	0.690030	
8	2.003783	-0.734125	1.551813	
6	2.222136	-0.906332	2.930951	
8	0.120424	1.271158	0.141141	
6	3.558942	1.371375	-0.977422	
6	3.926166	2.453868	-1.990210	
6	4.680869	1.103273	0.022726	
6	2.061449	2.604258	2.002918	

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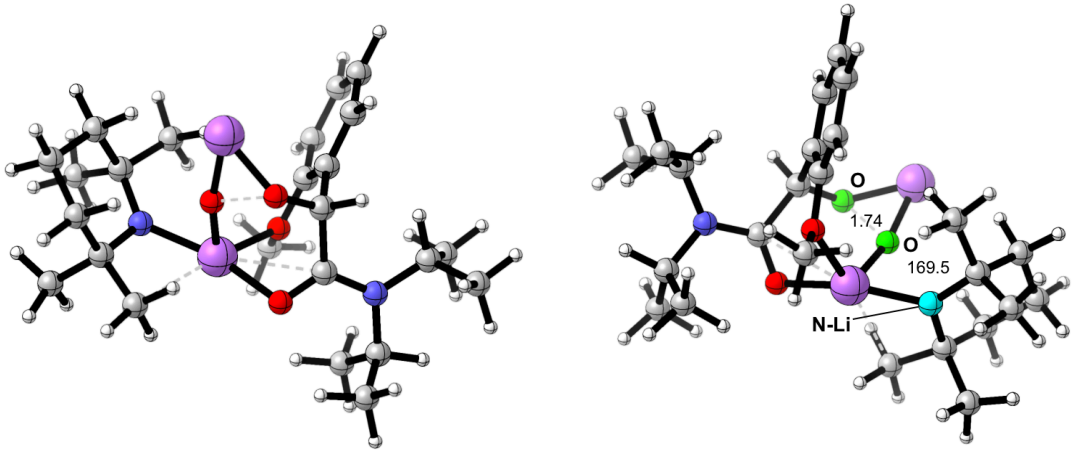
  3    -1.291932     0.037128     0.014638
  1     4.627762    -4.300123     0.455715
  1     3.654909    -2.783202     2.136919
  1     2.536961    -2.190072    -2.659841
  1     4.083169    -4.017152    -1.965811
  1     1.501355    -0.142880    -2.192718
  1     3.400874     0.448501    -1.542804
  1     4.958025     2.012810     0.577028
  1     4.380804     0.331429     0.746167
  1     5.576482     0.750983    -0.509042
  1     4.136788     3.419612    -1.507164
  1     4.830388     2.152722    -2.538478
  1     3.113833     2.596982    -2.717561
  1     3.281801     3.338144     0.426791
  1     1.078048     2.146447     2.170240
  1     2.839368     1.914912     2.362104
  1     2.123815     3.532153     2.590470
  1     1.459868     4.918791     0.524358
  1     1.479486     4.149930    -1.081188
  1     0.260636     3.656777     0.126064
  1     1.642083    -0.128334     3.440226
  1     1.871719    -1.894350     3.270268
  1     3.287527    -0.792231     3.192317
  1    -5.814021    -0.288935     2.185127
  1    -5.465848    -1.672435     1.127446
  1    -5.960417     0.136437    -2.115129
  1    -5.558998    -1.425792    -1.373937
  1    -7.166659    -0.217696     0.064785
  1    -6.088362     1.174425     0.165444
  1    -2.700594     1.787167    -1.507137
  1    -4.146779     1.794338    -2.550231
  1    -4.301534     2.137566    -0.818903
  1    -2.239771    -0.517557    -2.549383
  1    -3.463992    -1.813228    -2.401204
  1    -3.782021    -0.407941    -3.440781
  1    -3.268867    -2.209411     1.934770
  1    -2.075947    -0.921506     2.276216
  1    -3.570704    -1.034307     3.234445
  1    -4.003590     1.297123     2.786388
  1    -2.611629     1.502079     1.695772
  1    -4.243795     1.950013     1.156756
Energy        -1362.572170  (Hartree)
```

TS IV (from **C••LITMP** complex)

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Atom      X            Y            Z       (Angstrom)
  8     1.190188    -0.117107    -1.145685
```
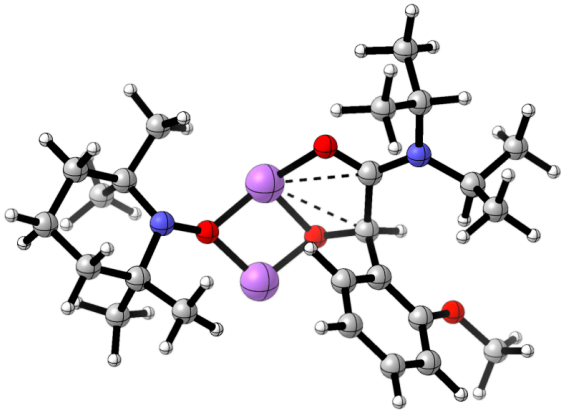

3	1.287227	1.024986	-2.454436
8	-0.166698	-0.044190	-2.239852
6	-1.308327	0.208643	-1.519555
6	-1.720406	-0.985520	-0.613813
7	-3.007478	-1.065563	-0.203522
6	-3.423872	-2.191466	0.658845
6	-3.298543	-3.540071	-0.045327
6	-1.263887	1.529432	-0.742231
6	-0.916765	1.644156	0.618753
6	-0.925605	2.892946	1.250018
6	-1.234264	4.042538	0.523456
6	-1.543719	3.956518	-0.831092
6	-1.559350	2.702568	-1.442527
8	-0.575365	0.505828	1.283411
6	-0.531418	0.524265	2.699061
8	-0.888776	-1.833139	-0.288058
3	0.733528	-0.851021	0.383403
6	-4.040680	-0.058794	-0.501267
6	-5.190833	-0.658821	-1.306412
6	-4.515346	0.640303	0.771138
6	-2.736999	-2.166306	2.021716
1	-1.228338	5.010004	1.028502
1	-0.669416	2.978718	2.305102
1	-1.831383	2.617722	-2.498697
1	-1.785630	4.852418	-1.404305
1	-2.120973	0.323460	-2.261272
1	-3.579247	0.711247	-1.124572
1	-5.027374	-0.051891	1.456613
1	-3.664905	1.095843	1.301537
1	-5.224678	1.439630	0.512020
1	-5.742302	-1.421458	-0.736507
1	-5.904267	0.131921	-1.579797
1	-4.815457	-1.119815	-2.231745
1	-4.493940	-2.025411	0.839230
1	-1.662404	-2.366023	1.925367
1	-2.876964	-1.189108	2.506371
1	-3.179742	-2.936118	2.671225
1	-3.757187	-4.324055	0.575213
1	-3.822084	-3.519677	-1.012655
1	-2.246808	-3.797266	-0.219582
1	-0.362554	-0.510221	3.020410
1	0.293500	1.150285	3.070260
1	-1.483895	0.887963	3.114890
6	3.393090	0.778988	0.544060
6	3.396662	-1.626784	-0.086438
6	4.186145	1.121237	-0.739233
6	4.153997	-1.293873	-1.389851
6	5.024838	-0.050228	-1.239406
1	4.818013	2.010457	-0.570821
1	3.458459	1.395808	-1.525723
1	4.761361	-2.156985	-1.713698
1	3.392559	-1.108342	-2.165844
1	5.503759	0.204547	-2.198868
1	5.847544	-0.247561	-0.531514
6	2.387758	1.907964	0.790436
1	1.649002	1.940294	-0.020266
1	1.843081	1.731053	1.731332
1	2.892894	2.884508	0.866817
6	4.369097	0.815527	1.750838
1	4.684458	1.850506	1.964006
1	3.863718	0.419154	2.645262
1	5.281505	0.228188	1.589397
6	2.380462	-2.736788	-0.392097

1	1.857357	-3.041291	0.532875
1	1.636335	-2.382214	-1.117037
1	2.880430	-3.632278	-0.793477
6	4.389804	-2.236391	0.936328
1	4.697734	-3.246129	0.617225
1	5.306550	-1.647076	1.062226
1	3.903950	-2.322227	1.920855
7	2.655942	-0.470421	0.416638

Energy -1362.511801 (Hartree)

4b-OLi••LiOTMP (complex from **TS IV**)

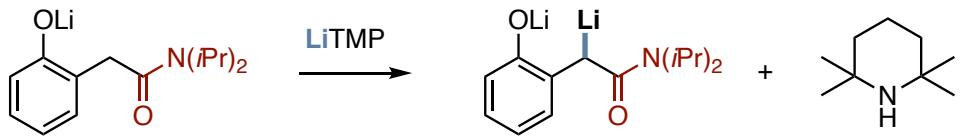


Atom	X	Y	Z	(Angstrom)
6	2.799558	-2.174288	-0.344453	
6	1.797007	-1.197483	-0.188131	
6	0.955862	-1.277205	0.922710	
6	1.092333	-2.286623	1.878450	
6	2.091670	-3.241994	1.712311	
6	2.945442	-3.191411	0.608189	
6	1.531330	-0.097310	-1.225664	
6	1.592049	1.261938	-0.462928	
8	0.532293	1.896628	-0.338977	
8	3.601539	-2.052253	-1.428454	
6	4.640789	-2.985969	-1.610603	
8	0.306712	-0.245557	-1.804578	
7	2.738484	1.699376	0.088276	
6	4.019917	0.991365	-0.064619	
6	4.498276	0.403200	1.261625	
6	2.738162	2.906071	0.941445	
6	1.855364	2.734181	2.175457	
6	2.420259	4.174538	0.154553	
6	5.071920	1.885510	-0.717750	
3	-1.041878	-1.318974	-1.286155	
8	-2.289008	-0.129768	-0.902160	
3	-0.914234	1.029766	-1.195618	
1	2.218247	-4.040316	2.445942	
1	3.720449	-3.948732	0.496317	
1	0.176429	-0.516541	1.043625	
1	0.425339	-2.322775	2.741154	
1	2.354769	-0.110429	-1.964204	
1	3.847260	0.157464	-0.750401	
1	4.761211	1.189532	1.986110	
1	3.724014	-0.239800	1.706585	
1	5.397731	-0.207654	1.092604	
1	5.340815	2.743687	-0.083738	
1	5.988455	1.304663	-0.895862	
1	4.711836	2.264256	-1.685326	
1	3.772604	2.995999	1.298513	

1	0.793920	2.696353	1.900922
1	2.114464	1.807182	2.708735
1	2.011697	3.579680	2.861461
1	2.556961	5.054643	0.800106
1	3.095116	4.274685	-0.708254
1	1.384665	4.160969	-0.207237
1	5.161145	-2.699093	-2.531579
1	5.354181	-2.963430	-0.770766
1	4.248167	-4.009167	-1.723789
6	-4.257669	1.093129	-0.548403
6	-3.896206	-1.221310	0.424635
6	-5.357245	1.337188	0.495815
6	-5.005192	-0.936497	1.449818
6	-6.044800	0.050715	0.934807
1	-6.084999	2.054333	0.083010
1	-4.893042	1.812683	1.376697
1	-5.474191	-1.891235	1.737698
1	-4.533672	-0.518025	2.355242
1	-6.786523	0.264062	1.719782
1	-6.602552	-0.388897	0.092174
6	-3.447526	2.387746	-0.702646
1	-2.828089	2.556992	0.191530
1	-2.801514	2.357951	-1.594077
1	-4.123388	3.247572	-0.827491
6	-4.861335	0.750477	-1.922124
1	-5.231948	1.663804	-2.413369
1	-4.078725	0.308625	-2.555280
1	-5.702397	0.048200	-1.857529
6	-2.772839	-1.978178	1.145832
1	-2.043362	-2.418994	0.447291
1	-2.239860	-1.299677	1.827993
1	-3.191814	-2.812707	1.728960
6	-4.419265	-2.117731	-0.713286
1	-4.484945	-3.163272	-0.373806
1	-5.416229	-1.822883	-1.064286
1	-3.727643	-2.075274	-1.567920
7	-3.336441	0.072115	-0.011005

Energy -1362.652026 (Hartree)

LiTMP-promoted enolization of compounds 2

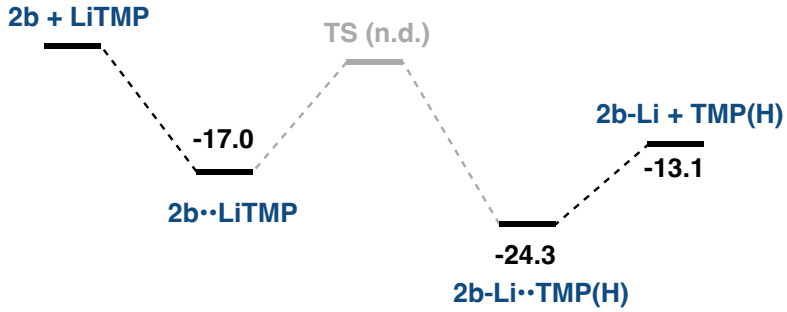


2b
(*lithium phenoxide*)

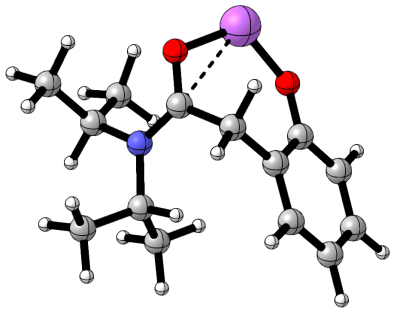
2b-Li

TMP(H)

Energies and cartesian coordinates



2b (lithium phenoxide)

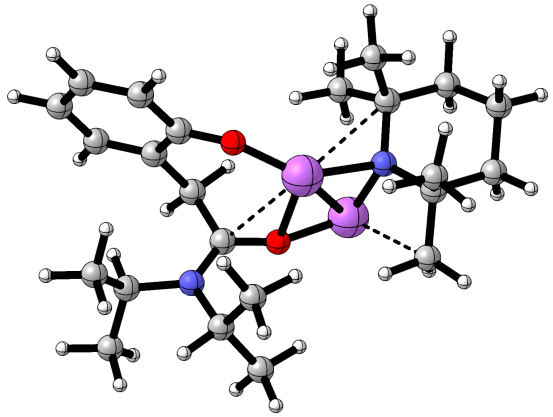


Atom	X	Y	Z	(Angstrom)
6	3.824757	0.384498	0.863463	
6	3.142907	-0.825034	0.935466	
6	2.025447	-1.108871	0.102418	
6	1.628798	-0.077205	-0.808448	
6	2.337288	1.122758	-0.871279	
6	3.434767	1.374079	-0.044832	
1	4.677768	0.558878	1.524512	
1	3.451576	-1.601141	1.639650	
1	2.015378	1.885559	-1.587921	
1	3.974026	2.320062	-0.109737	
8	1.398792	-2.235998	0.162123	
6	0.435316	-0.342999	-1.698111	
1	0.259848	0.510413	-2.367986	
6	-0.836546	-0.677813	-0.921091	
8	-1.289686	-1.839023	-0.973302	
7	-1.431340	0.256553	-0.165952	
6	-2.572635	-0.111996	0.700738	
6	-2.212994	-1.189573	1.722572	
6	-3.822104	-0.452626	-0.105718	
1	-2.788818	0.800178	1.271183	
1	-2.978588	-1.209888	2.511822	

1	-2.169634	-2.184991	1.263269
1	-1.242202	-0.971495	2.192033
1	-4.086667	0.373277	-0.781850
1	-3.664501	-1.360883	-0.700954
1	-4.667924	-0.620676	0.577093
6	-0.972914	1.655819	-0.094166
6	-0.369666	1.968776	1.272450
6	-2.085280	2.626037	-0.483998
1	-0.178567	1.765353	-0.836475
1	0.047328	2.986396	1.268832
1	-1.124495	1.918625	2.072296
1	0.442605	1.264553	1.506989
1	-2.919171	2.616705	0.233451
1	-1.682192	3.648547	-0.509058
1	-2.479045	2.387631	-1.482712
3	-0.032848	-3.044331	-0.373110
1	0.615496	-1.224893	-2.330784

Energy -757.501996 (Hartree)

2b••LiTMP (complex)

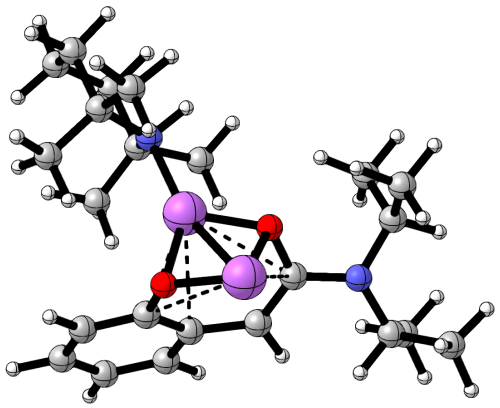


Atom	X	Y	Z	(Angstrom)
6	-3.374868	-3.430278	-1.167790	
6	-2.178692	-2.792127	-1.476014	
6	-1.581462	-1.848886	-0.593674	
6	-2.280257	-1.587762	0.628642	
6	-3.476575	-2.243062	0.917154	
6	-4.040337	-3.166792	0.034001	
1	-3.797767	-4.146580	-1.877100	
1	-1.660074	-2.998827	-2.415054	
1	-3.986329	-2.014875	1.858850	
1	-4.977344	-3.668926	0.278363	
8	-0.478303	-1.245157	-0.877897	
6	-1.686637	-0.572303	1.579198	
1	-2.377261	-0.383034	2.414288	
6	-1.314102	0.739205	0.902821	
8	-0.107819	1.094001	0.891384	
7	-2.242577	1.484111	0.304998	
6	-1.853998	2.647493	-0.526095	
6	-0.979896	2.242550	-1.710698	
6	-1.263962	3.791633	0.292076	
1	-2.801183	3.005788	-0.947750	
1	-0.943882	3.070459	-2.433268	
1	0.052504	2.029521	-1.402583	
1	-1.392053	1.357253	-2.214927	
1	-1.932032	4.063164	1.122189	
1	-0.281864	3.523678	0.701452	
1	-1.144237	4.674541	-0.352552	

6	-3.689665	1.196705	0.395962
6	-4.260045	0.763150	-0.950433
6	-4.440811	2.379712	1.001906
1	-3.800139	0.358314	1.088027
1	-5.318222	0.490660	-0.827547
1	-4.207342	1.571071	-1.696106
1	-3.721704	-0.114571	-1.337619
1	-4.423916	3.265988	0.350654
1	-5.493087	2.098862	1.150602
1	-4.017614	2.653231	1.979280
3	0.823379	-0.130834	-0.485777
1	-0.745009	-0.943856	2.009292
6	3.575413	0.972110	-0.448174
6	3.149630	-1.310383	0.515284
3	1.600912	0.956481	1.553670
7	2.677699	0.056241	0.262183
6	3.076710	-2.247534	-0.714421
1	3.289643	-3.290243	-0.426579
1	2.063785	-2.222370	-1.149179
1	3.793172	-1.974064	-1.499736
6	3.614215	0.759358	-1.979608
1	2.587577	0.719272	-2.381836
1	4.142914	1.584628	-2.484317
1	4.119662	-0.173121	-2.262614
6	3.038716	2.393823	-0.223502
1	3.664126	3.150424	-0.721964
1	2.014481	2.496238	-0.619321
1	3.026228	2.647514	0.852375
6	2.212138	-1.918548	1.567747
1	1.181902	-1.982333	1.176941
1	2.522808	-2.937021	1.849073
1	2.206083	-1.306606	2.487144
6	5.015576	0.922973	0.105877
1	5.009618	1.375394	1.114147
1	5.682475	1.539975	-0.519870
6	4.586069	-1.329019	1.076430
6	5.542022	-0.502716	0.223449
1	4.563224	-0.899650	2.094680
1	4.941661	-2.368852	1.171914
1	5.643473	-0.954462	-0.777655
1	6.550876	-0.502560	0.665638

Energy -1173.148167 (Hartree)

2b-Li••TMP(H) (complex)



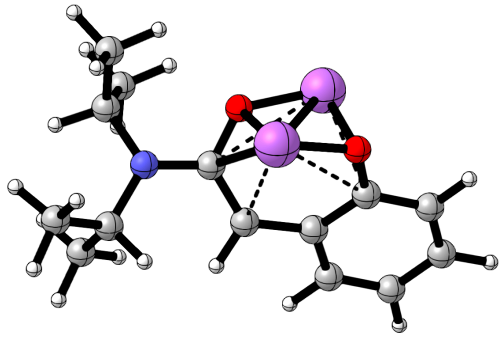
Atom	X	Y	Z	(Angstrom)
6	-1.560638	4.014054	-0.147582	
6	-1.359215	3.094122	-1.169288	

6	-0.285180	2.172525	-1.162567
6	0.631660	2.194156	-0.054694
6	0.392492	3.149830	0.958562
6	-0.674641	4.041599	0.934095
1	-2.401369	4.709727	-0.195642
1	-2.026493	3.061373	-2.033923
1	1.089613	3.179230	1.801105
1	-0.810331	4.755347	1.748713
8	-0.168779	1.302771	-2.150492
6	1.850529	1.373322	0.077409
1	2.612997	1.842487	0.698525
6	2.089791	0.064491	-0.320291
8	1.191323	-0.689117	-0.905780
7	3.343997	-0.535187	-0.175587
6	3.406456	-1.984753	0.075946
6	3.309408	-2.818199	-1.201273
6	2.410821	-2.451859	1.138422
1	4.408833	-2.157881	0.492919
1	3.517656	-3.877609	-0.984727
1	2.304195	-2.734786	-1.634307
1	4.043308	-2.471791	-1.944524
1	2.493375	-1.835928	2.047083
1	1.382191	-2.380435	0.762120
1	2.614419	-3.497828	1.413550
6	4.512117	0.251015	0.220799
6	5.775399	-0.212203	-0.505659
6	4.721389	0.287274	1.736513
1	4.316320	1.273828	-0.126194
1	6.604076	0.476099	-0.283235
1	6.093119	-1.218848	-0.195143
1	5.617281	-0.218059	-1.594041
1	4.971687	-0.713891	2.122296
1	5.549696	0.962282	1.999314
1	3.815134	0.636951	2.252599
3	1.293692	0.330093	-2.471468
3	-0.560184	-0.112672	-0.903475
7	-2.072763	-1.114145	-0.007509
6	-2.332900	-0.681663	1.396440
6	-3.218445	-1.267269	-0.946592
6	-3.497616	-1.485720	1.997794
6	-1.043945	-0.971455	2.166783
6	-2.608813	0.822142	1.489228
6	-4.373287	-2.035553	-0.281741
6	-2.684952	-2.073822	-2.131873
6	-3.683182	0.094408	-1.472620
6	-4.729722	-1.484907	1.096327
1	-3.163372	-2.528477	2.143014
1	-3.737115	-1.082927	2.994569
1	-0.204702	-0.376289	1.767955
1	-1.169887	-0.716079	3.228874
1	-0.777210	-2.038417	2.102313
1	-2.551670	1.131346	2.543598
1	-1.855144	1.395347	0.929341
1	-3.602261	1.104686	1.120359
1	-4.067112	-3.091083	-0.171989
1	-5.247781	-2.023374	-0.951413
1	-3.493743	-2.282846	-2.846702
1	-1.897527	-1.518367	-2.668079
1	-2.266382	-3.036143	-1.797622
1	-2.822486	0.685757	-1.824917
1	-4.361632	-0.058244	-2.325155
1	-4.224195	0.685648	-0.724191
1	-5.134759	-0.464107	1.005182

1	-5.526164	-2.095047	1.547831
1	-1.657238	-2.047027	0.072384

Energy -1173.160790 (Hartree)

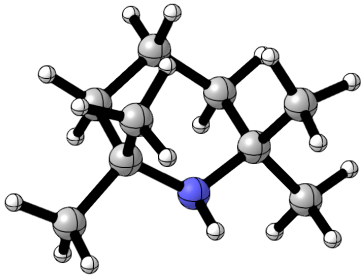
2b-Li



Atom	X	Y	Z	(Angstrom)
6	4.054353	1.501812	0.673718	
6	4.752235	0.356578	0.280030	
6	4.058386	-0.704394	-0.291073	
6	2.660964	-0.666210	-0.500293	
6	1.930951	0.486349	-0.055934	
6	2.674078	1.547525	0.503098	
8	2.055218	-1.692318	-1.084104	
6	0.475854	0.679473	-0.207781	
6	-0.538266	-0.251774	-0.020616	
7	-1.887755	0.070284	-0.177470	
6	-2.289310	1.379253	-0.693895	
6	-3.513100	1.273700	-1.604449	
8	-0.302727	-1.518380	0.216100	
6	-2.885989	-0.663517	0.619368	
6	-3.270409	-2.008199	0.004250	
6	-2.498270	-0.794681	2.092582	
6	-2.500378	2.416343	0.411081	
3	0.339938	-1.491748	-1.599363	
3	1.309203	-2.283211	0.509842	
1	5.835002	0.294407	0.409294	
1	4.582898	-1.599733	-0.633269	
1	2.126830	2.439886	0.820342	
1	4.579685	2.350272	1.115825	
1	0.181171	1.726636	-0.267786	
1	-3.786204	-0.033431	0.593299	
1	-3.342533	-1.200447	2.669960	
1	-1.638182	-1.465843	2.213893	
1	-2.237065	0.187971	2.513474	
1	-3.564647	-1.879925	-1.048372	
1	-2.424170	-2.705341	0.050000	
1	-4.123145	-2.446612	0.545471	
1	-1.462898	1.716752	-1.332587	
1	-2.710703	3.406658	-0.019825	
1	-3.355264	2.141187	1.049200	
1	-1.608120	2.500722	1.048912	
1	-4.423266	0.989472	-1.055680	
1	-3.706476	2.247892	-2.077058	
1	-3.342568	0.534409	-2.400717	

Energy -764.464107 (Hartree)

TMP(H)



Atom	X	Y	Z	(Angstrom)
6	-1.279130	-0.255785	-0.059058	
6	-1.250134	1.235472	-0.426201	
6	1.249937	1.235338	-0.426614	
6	1.279164	-0.255763	-0.059055	
7	0.000036	-0.851208	-0.466788	
6	-2.361125	-0.960430	-0.880684	
1	-2.414293	-2.028708	-0.614237	
1	-3.350388	-0.515606	-0.695068	
1	-2.131618	-0.885889	-1.953176	
6	-1.624181	-0.438826	1.430890	
1	-2.678405	-0.177807	1.612145	
1	-1.480730	-1.489685	1.728612	
1	-1.011448	0.188126	2.090964	
6	1.624079	-0.438411	1.430970	
1	1.480844	-1.489243	1.728875	
1	2.678243	-0.177123	1.612182	
1	1.011168	0.188535	2.090869	
6	2.361336	-0.960504	-0.880405	
1	3.350538	-0.515611	-0.694617	
1	2.414505	-2.028746	-0.613862	
1	2.132044	-0.886039	-1.952951	
1	0.000026	-1.845755	-0.238824	
6	0.000046	1.939678	0.093979	
1	-1.269998	1.318257	-1.526127	
1	-2.164160	1.718218	-0.045265	
1	0.000010	2.992142	-0.227994	
1	0.000222	1.952855	1.196191	
1	1.269070	1.317595	-1.526622	
1	2.164166	1.718315	-0.046502	

Energy -408.658903 (Hartree)

X-Ray Structural Data for **3a**

Table S4. Crystal data and structure refinement for **3a**

Identification code	**3a** (CCDC 2475367)
Empirical formula	$C_{15}H_{23}NO_3$
Formula weight	265.34
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4288(5)
b/Å	12.6625(7)
c/Å	13.1745(7)
α/°	90
β/°	95.224(5)
γ/°	90
Volume/Å^3	1566.41(15)
Z	4
ρ_{calcg}/cm^3	1.125
μ/mm^{-1}	0.078
F(000)	576.0
Crystal size/mm^3	0.11 × 0.1 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.996 to 59.3
Index ranges	-13 ≤ h ≤ 12, -16 ≤ k ≤ 17, -18 ≤ l ≤ 17
Reflections collected	25743
Independent reflections	4101 [R_{int} = 0.0404, R_{sigma} = 0.0333]
Data/restraints/parameters	4101/33/182
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1512
Final R indexes [all data]	R_1 = 0.1034, wR_2 = 0.1721
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15

Table S5. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2475367. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	931.8(14)	2401.2(11)	9181.8(9)	61.3(4)

Table S5. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2475367. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O3	-2424.4(13)	2345.5(11)	5953.6(9)	62.0(4)
C6	403.8(16)	3016.4(13)	7504.7(12)	41.5(4)
O2	-74.0(16)	1431.6(12)	6520.5(11)	67.6(4)
N1	-2921.9(14)	2949.8(13)	7493.7(10)	52.8(4)
C7	598.4(18)	3763.5(15)	6760.7(13)	51.7(4)
C5	1163.9(17)	3128.9(13)	8455.2(12)	46.9(4)
C9	-2086.3(17)	2482.0(13)	6874.5(11)	44.3(4)
C8	-588.1(17)	2095.6(13)	7275.8(12)	45.3(4)
C4	2090(2)	3969.0(16)	8631.1(16)	61.9(5)
C2	1525(2)	4609.7(16)	6928.6(17)	63.0(5)
C10	-2503(2)	3093(2)	8596.2(14)	72.3(6)
C3	2263(2)	4695.8(17)	7874.8(18)	70.1(6)
C13	-4332(2)	3383(2)	7093.5(15)	73.4(6)
C1	1725(3)	5400(2)	6100(2)	101.0(9)
C14	-4170(3)	4267(2)	6335(2)	96.0(8)
C12	-3532(3)	2511(4)	9223.8(19)	138.6(15)
C15	-5357(2)	2518(3)	6698(2)	99.5(9)
C11	-2303(4)	4247(3)	8862(2)	131.7(13)

Table S6. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2475367. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	67.2(8)	74.8(9)	38.3(7)	6.5(6)	-15.3(6)	-5.1(7)
O3	55.9(7)	91.2(10)	36.1(6)	-10.2(6)	-11.1(5)	8.3(7)
C6	38.6(8)	49.2(9)	36.2(8)	-2.2(7)	0.1(6)	5.1(6)
O2	66.4(9)	72.7(9)	60.6(9)	-23.4(7)	-10.2(7)	19.8(7)
N1	42.9(8)	78.3(10)	36.4(7)	-1.2(7)	-0.8(6)	4.4(7)
C7	46.3(9)	66.2(11)	42.6(9)	7.4(8)	3.8(7)	5.3(8)
C5	43.6(9)	54.9(10)	41.0(8)	-1.8(7)	-2.4(7)	5.0(7)
C9	44.9(8)	52.2(9)	34.6(8)	-0.4(7)	-3.7(6)	-3.9(7)
C8	49.9(9)	48.3(9)	36.4(8)	-2.4(7)	-4.1(7)	5.1(7)
C4	53.1(10)	70.5(12)	59.8(11)	-11.6(10)	-7.7(9)	-6.0(9)
C2	49.2(10)	63.4(12)	78.0(13)	14.1(10)	13.7(9)	-1.0(9)
C10	57.7(11)	123.5(19)	35.5(9)	-9.5(11)	2.6(8)	14.3(11)
C3	54.6(11)	62.1(12)	93.1(16)	-5.8(12)	4.0(11)	-13.0(9)
C13	50.7(11)	118.0(19)	50.5(11)	-4.9(12)	-1.2(8)	23.4(11)
C1	86.5(18)	97.7(19)	120(2)	42.0(17)	17.7(15)	-11.6(14)
C14	102.4(19)	97.3(18)	85.6(17)	5.6(15)	-6.1(14)	43.4(15)
C12	79.7(18)	286(5)	52.2(14)	28(2)	17.8(13)	-4(2)
C15	46.3(12)	170(3)	80.2(17)	2.4(17)	-5.7(11)	-9.4(15)
C11	142(3)	146(3)	100(2)	-72(2)	-30.6(19)	49(2)

Table S7. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.361(2)	C5	C4	1.383(3)
O3	C9	1.2382(19)	C9	C8	1.542(2)
C6	C7	1.386(2)	C4	C3	1.377(3)
C6	C5	1.392(2)	C2	C3	1.376(3)
C6	C8	1.508(2)	C2	C1	1.505(3)
O2	C8	1.421(2)	C10	C12	1.521(4)
N1	C9	1.324(2)	C10	C11	1.511(4)
N1	C10	1.481(2)	C13	C14	1.517(4)
N1	C13	1.490(2)	C13	C15	1.521(4)
C7	C2	1.387(3)			

Table S8. Bond Angles for **3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	C6	C5	118.40(16)	O2	C8	C6	110.65(14)
C7	C6	C8	120.39(14)	O2	C8	C9	107.93(13)
C5	C6	C8	121.20(15)	C3	C4	C5	120.50(18)
C9	N1	C10	122.54(14)	C7	C2	C1	121.1(2)
C9	N1	C13	120.56(14)	C3	C2	C7	117.72(18)
C10	N1	C13	116.88(15)	C3	C2	C1	121.2(2)
C6	C7	C2	122.43(17)	N1	C10	C12	110.3(2)
O1	C5	C6	117.44(15)	N1	C10	C11	111.2(2)
O1	C5	C4	122.87(15)	C11	C10	C12	114.5(3)
C4	C5	C6	119.68(16)	C2	C3	C4	121.28(18)
O3	C9	N1	123.47(15)	N1	C13	C14	111.38(19)
O3	C9	C8	115.95(14)	N1	C13	C15	112.0(2)
N1	C9	C8	120.56(13)	C14	C13	C15	113.8(2)
C6	C8	C9	110.81(13)				

Table S9. Torsion Angles for **3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C5	C4	C3	-178.62(18)	C9	N1	C10	C12	-118.4(2)
O3	C9	C8	C6	107.17(17)	C9	N1	C10	C11	113.4(2)
O3	C9	C8	O2	-14.1(2)	C9	N1	C13	C14	-63.1(3)
C6	C7	C2	C3	-0.2(3)	C9	N1	C13	C15	65.7(2)
C6	C7	C2	C1	179.24(19)	C8	C6	C7	C2	-178.45(16)
C6	C5	C4	C3	0.2(3)	C8	C6	C5	O1	-2.7(2)
N1	C9	C8	C6	-71.4(2)	C8	C6	C5	C4	178.43(16)
N1	C9	C8	O2	167.30(16)	C10	N1	C9	O3	179.20(19)
C7	C6	C5	O1	178.48(15)	C10	N1	C9	C8	-2.3(3)
C7	C6	C5	C4	-0.4(2)	C10	N1	C13	C14	115.5(2)
C7	C6	C8	O2	64.68(19)	C10	N1	C13	C15	-115.7(2)
C7	C6	C8	C9	-55.00(19)	C13	N1	C9	O3	-2.3(3)
C7	C2	C3	C4	-0.1(3)	C13	N1	C9	C8	176.16(17)
C5	C6	C7	C2	0.4(3)	C13	N1	C10	C12	63.0(3)
C5	C6	C8	O2	-114.12(17)	C13	N1	C10	C11	-65.1(3)
C5	C6	C8	C9	126.19(16)	C1	C2	C3	C4	-179.5(2)
C5	C4	C3	C2	0.0(3)					

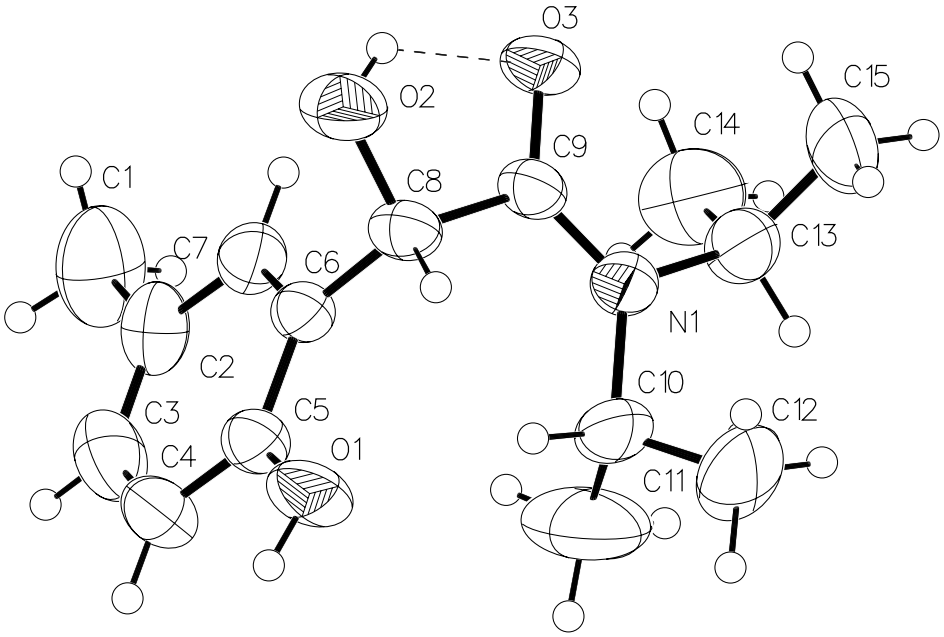


Figure S11. X-Ray structure of **3a** with thermal ellipsoids drawn at 50% probability level. (*S*)-enantiomer is shown.

References

1. W. G. Kofron and L. M. Baclawski, *J. Org. Chem.*, 1976, **41**, 1879-1880.
2. J. A. Grzyb, M. Shen, C. Yoshina-Ishii, W. Chi, R. S. Brown and R. A. Batey, *Tetrahedron*, 2005, **61**, 7153-7175.
3. D. Dailler, R. Rocaboy and O. Baudoin, *Angew. Chem. Int. Ed.*, 2017, **56**, 7218-7222.
4. S. Ghinato, F. De Nardi, P. Bolzoni, A. Antenucci, M. Blangetti and C. Prandi, *Chem. Eur. J.*, 2022, **28**, e202201154.
5. J. Clayden, J. H. Pink, N. Westlund and F. X. Wilson, *Tetrahedron Lett.*, 1998, **39**, 8377-8380.
6. J. Clayden, M. Helliwell, C. McCarthy and N. Westlund, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3232-3249.
7. F. Bertrand, D. A. Basketter, D. W. Roberts and J.-P. Lepoittevin, *Chem. Res. Toxicol.*, 1997, **10**, 335-343.
8. N. Truchan, C. Jandl, A. Pöthig, S. Breitenlechner and T. Bach, *Synthesis*, 2019, **51**, 3060-3076.
9. A. Sahari, J. Puumi, J. K. Mannisto and T. Repo, *J. Org. Chem.*, 2023, **88**, 3822-3829.
10. J. Fässler, J. A. McCubbin, A. Roglans, T. Kimachi, J. W. Hollett, R. W. Kunz, M. Tinkl, Y. Zhang, R. Wang, M. Campbell and V. Snieckus, *J. Org. Chem.*, 2015, **80**, 3368-3386.
11. (a) J. G. Hill, B. E. Rossiter and K. B. Sharpless, *J. Org. Chem.*, 1983, **48**, 3607-3608; (b) M. Möller, M. Husemann and G. Boche, *J. Organomet. Chem.*, 2001, **624**, 47-52.
12. V. Rathore, M. Sattar, R. Kumar and S. Kumar, *J. Org. Chem.*, 2016, **81**, 9206-9218.
13. J. Bai, B. K. Zambron and P. Vogel, *Org. Lett.*, 2014, **16**, 604-607.
14. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
15. (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654; (b) A. McLean and G. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639-5648.
16. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
17. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3094.
18. Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.